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TECHNOLOGIES FOR REDUCING DIOXIN IN THE MANUFACTURE OF BLEACHED WOOD PULP

Background Paper

CONGRESS OF THE UNITED STATES OFFICE OF TECHNOLOGY ASSESSMENT

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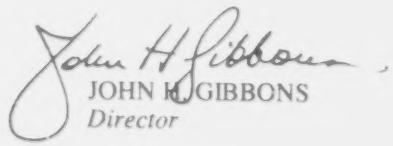
Foreword

As analytical technology improves, we are discovering dioxins associated with many products commonly found in the home and workplace. Recently, dioxins have been detected in wastes resulting from the manufacture of wood pulp. Paper products made from wood pulp are used in tremendous volumes for food packaging, hygienic products, printing paper, writing paper, paperboard for shipping containers, and numerous other household items. Between 650 and 700 pounds of paper products are used annually by each American, with domestic and foreign consumption continuing to rise at a steady rate.

Most of the paper used in the United States is white paper made from bleached wood pulp. Chlorine is commonly used as a bleach. It has been found that bleaching can result in the formation of dioxin in the pulp when chlorine reacts with organic constituents of wood. Although preliminary surveys have detected dioxin in pulp mill wastes, the scope of the problem is not yet known. Studies currently under way by the Environmental Protection Agency, the Food and Drug Administration, the Consumer Products Safety Commission, the National Institute for Occupational Safety and Health, and the U.S. paper industry will shed light on this when completed later in 1989.

Alternative technologies using oxygen as a pretreatment to chlorine bleaching and improved delignification that removes more of the potential reactants from the wood can reduce the amount of dioxin in bleached pulp. Substituting other bleaching chemicals for chlorine also shows promise for reducing the amount of dioxin produced in the bleaching process should regulation be required. This study provides an assessment of these technologies; it does not address the policy issues related to regulating dioxin in paper products and controlling environmental release.



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NOTE: OTA is grateful for the valuable assistance and thoughtful critiques provided by the workshop participants. The views expressed in this OTA background paper, however, are the sole responsibility of the Office of Technology Assessment.

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Introduction, Summary, and Findings

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Chapter 1

Introduction, Summary, and Findings

PURPOSE AND SCOPE

"Dioxin" is the term used in referring to the family of 210 chlorinated chemicals known as chlorinated dibenzo-para-dioxins and chlorinated dibenzofurans. The most toxic member of this large family of compounds is 2,3,7,8-tetrachloro-p-dibenzodioxin (2,3,7,8-TCDD or TCDD); the closely related compound 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF or TCDF) is believed to be about one-tenth as potent. Both of these chemicals can be formed during the manufacture of bleached wood pulp if chlorine is used as a bleaching agent. The amount of TCDD and TCDF formed in the bleaching process is measured in parts per trillion (ppt). The relative toxicity of these chemicals is measured in ppt and expressed as "Toxic Equivalents" (TEQs) using TCDD as the standard. TCDD is considered to be highly toxic based on laboratory animal experiments and has been linked to malignancies, birth defects, and physical deterioration in animals. Evidence of human health effects is less certain and remains a contentious issue among scientists. The U.S. Environmental Protection Agency (EPA) classifies it as a "probable human carcinogen."

The release of EPA's National Dioxin Study in 1987 focused attention on evidence that showed a pattern of dioxin concentrations in stream bottom sediment and fish below pulp mill waste outfalls. Subsequent studies by the paper industries and government agencies in North America and Europe have confirmed that detectable amounts of TCDD and TCDF are produced and released into the environment at many bleached kraft pulp mills. Measurements of dioxin levels in the three sources of pollution (pulp, effluent, and sludge) are being conducted at all U.S. chemical pulp mills using chlorine bleach under the joint sponsorship of EPA and the American paper industry. The results of these studies and others underway in Canada and Europe will contribute much more to the information base now available, but final results are months away.

Bleached wood pulp is used in paper products such as writing and printing papers, rayon, tissues, towels, disposable diapers, food packaging, and a myriad of other products. Paper is used so widely in modern societies that every person comes in contact with bleached paper products almost daily. The knowledge that TCDD and TCDF are produced and released during the manufacture of chlorine-bleached kraft pulp has prompted action by the Federal agencies charged with protecting health and the environment and has stimulated research by a paper industry faced with increasing public concern and, as a consequence, possible regulatory action.

Environmental and consumer groups have organized an international action program to inform the public, prompt consumer action, and stimulate political and regulatory action in the pulp-producing countries of North America and Europe. The United Paperworkers International Union, the labor union that represents many of the paper mill employees in North America, and the National Institute for Occupational Health (NIOSH) are monitoring the potential health impacts of exposure of workers to dioxin in pulp and paper mills.

This study reviews what is known about the production and fate of TCDD and TCDF and other associated chlorinated compounds during the course of pulp bleaching and brightening. The study is specifically aimed at assessing the state of pulping and bleaching technologies that show promise for reducing the amount of those chemicals resulting from the manufacture of bleached kraft pulp, such as extended delignification, oxygen delignification, the use of bleaching chemicals that might substitute for some or all of the chlorine commonly used, modifications of the timing, amount, and operating

conditions of the chlorine bleach sequence, and a review of pulping and/or bleaching technologies that are not yet commercially available, but might be in the future.

Because this is a technical background report, neither an assessment of policy options related to the need for regulatory action, nor the form such regulations might take, are included. Furthermore, this assessment assumes—based on past trends and industry projections—that a strong demand for high-brightness bleached pulp and paper products will continue in the future. Should the public boycott or avoid the use of bleached paper products in the future because of a perceived health risk, the paper industry would have to adjust to the changing markets within its own constraints.

Markets for unbleached hygienic paper products, disposable diapers, coffee filters, and milk cartons, for example, have developed in Sweden where "environment-graded" or "environment-positive" lines of unbleached paper products are retailed along with bleached grades. Recently, the Canadian pulp and paper industry has agreed to reduce the amount of dioxin in paper stock used for milk containers after Health and Welfare Canada, a government agency, discovered trace amounts of dioxin leaching into milk from plastic-coated paper cartons. The pulp and paper industry claims that paper products requiring high strength and long-term durability generally must be made with a highly bleached pulp, and industry analysts believe that this will likely continue to be a major proportion of the pulp produced.

Market pulp is a commodity traded widely in world markets. The possibility exists that some countries in the future may impose limits on the amount of residual chlorine compounds or dioxin in pulp and paper products that can be imported. If similar collective action were to be taken by a large number of trading partners, such as the European Economic Community or a coalition of Pacific Rim countries, a significant portion of North America's export market could be affected. If such trade restrictions were broadly adopted, it could, for practical purposes, impose de facto international performance standards on those firms wanting to compete in international markets.

OTA convened a workshop in November 1988 to discuss the latest information regarding three aspects of dioxin and bleached wood pulp manufacture:

1. What is known about the distribution and effects of TCDD and TCDF resulting from environmental releases by pulp mills?
2. What is known about the amount of residual TCDD and TCDF in paper products, and what is the level of risk to consumers and mill workers?
3. What is the current understanding of the precursors that react with chlorine to form TCDD and TCDF, and what is known about the means to reduce their formation?

As a result of the workshop, we were impressed by how fast knowledge about TCDD and TCDF in bleached wood pulp is accumulating. This report is only a "snapshot" of the technology and knowledge about the formation of dioxin and possible means to reduce it as of December 1988.

THE U.S. PULP AND PAPER INDUSTRY

The United States leads the world in per capita paper consumption. In 1986 U.S. consumers used over 660 pounds of paper products per person.[1] This new record of paper consumption continues the steady increase in the domestic use of paper that saw per capita consumption rise about 16 percent between 1976 and 1986. Paper, which is indirectly correlated with gen-

[1]American Paper Institute, *1987 Statistics of Paper, Paperboard & Wood Pulp* (New York, NY:Associated Press International, 1987), p. 2.

eral economic activity, is currently being consumed at the rate of about 21,000 tons per billion dollars of the real gross national product (GNP) generated. For a variety of reasons, including the reduction of solid waste, efforts to recycle scrap paper are expanding, particularly in urban areas.

Nearly 73 million tons of paper, board, and construction board were produced in the United States in 1986.[2] Although 4.8 million tons of paper products were exported by U.S. producers, almost 12 million tons were imported for domestic consumption. Most of the imports originated in Canada and were newsprint. More than 70 percent of U.S. exports and 80 percent of imports in 1987 were bleached or semi-bleached pulps.[3]

Pulp products valued at $3.9 billion were shipped from U.S. pulpmills in 1987. The paper and allied products industry (SIC 26) employed over 674,000 persons in 1986, with about one-third of those directly involved in the production of paper and pulp (SIC 261, 262, 266).[4] In general, pulp mills have tended to concentrate in the South and Northwest near major sources of wood, while allied industries and conversion facilities are more broadly distributed near primary markets.

Future prospects for the pulp and paper industry are bright. In the Pacific Rim countries where industrial expansion is expected to increase dramatically, forest-deficient countries like Japan, Korea, and Taiwan are considered large potential markets. The United States and Canada, with their vast forest resources, their established industries, and technological capacity, are well positioned to take advantage of new export markets. However, international competition for new markets is sharpening, with overseas suppliers in Brazil, Portugal, Spain, Morocco, and South Africa expanding their capacity.

SUMMARY

The Pulp and Paper Making Process

The manufacture of pulp and paper involves the separation and purification of cellulosic wood fibers from which paper is formed. About half of the wood raw material is cellulosic fiber, and half is lignin, hemicellulose, and other extractive compounds that cement and strengthen the fibers. The pulping process involves either the use of chemicals, heat, and pressure in a digester to dissolve the lignin and free the fibers from one another or, in the case of mechanical pulp and chemical-mechanical pulp, the abrasion of wood in a grinder or refiner to physically tear the fibers apart.

Pulping and bleaching technology must be matched to the quality and characteristics of the pulp and paper to be produced. No single pulping or bleaching process can produce pulp suitable for all uses.

To produce purified cellulose and white pulps, lignin and other colored extractives carried forward from the digester must be removed or brightened in successive bleaching stages using chlorine and/or other oxidative chemicals. It is in the bleaching processes where most chlorinated organic contaminants, including dioxin, originate. A wide range of bleaching sequences and caustic washing stages may be used to bleach and brighten pulp. The choice of which bleaching agents and in what sequence is generally determined by pulp characteristics desired, such as brightness and strength, balanced against capital and operating costs.

[2]Ibid.

[3]U.S. Department of Commerce, *1988 U.S. Industrial Outlook* (Washington, DC: International Trade Administration, 1988), p. 6-3.

[4]American Paper Institute, op. cit., note 1, p. 54. NOTE: "SIC" refers to "Standard Industrial Code," a classification of U.S. industries used by the U.S. Department of Commerce.

Several pulping processes are still at the precommercial or pilot plant stage. Most are not "new" in the sense of time, they are new because they have not yet been accepted by the industry. These include soda/anthroquinone, organosolv techniques (ester pulping), hydrotropic pulping, and closed-cycle processes. Research is also underway on biological pulping processes, but they will likely compete with mechanical processes rather than chemical pulps.

New pulping technologies are emerging, but their acceptance will depend on efficiency, pulp quality, cost effectiveness, or other factors that make them competitive with conventional technology. To the extent that new pulping systems might reduce the amount of residual lignin carried over to the bleaching process, the amount of chemical bleaching required to attain the desired brightness might be reduced and subsequently the amount of chlorine used as a bleaching agent trimmed.

Environmental Considerations

Effluents from bleached pulp mills contain a variety of substances, some of which are known or suspected of being toxic, genotoxic, mutagenic, or teratogenic. Chlorinated organics, including TCDD and TCDF, that appear to be produced in the chlorine bleaching and delignification processes, are of particular concern. The composition of bleaching effluent is extremely complex and varies widely from mill to mill. The chlorinated components of the waste stream consist of a variety of compounds, including simple phenols, high and low molecular weight polymers, and neutral and acidic materials from the breakdown of the phenolic rings in lignin. An average North American pulp mill produces between 35 and 50 tons of chlorinated substances daily. Greenpeace International, the Environmental Defense Fund, and other environmental organizations advocate immediately minimizing and eventually eliminating the use of chlorine in order to avoid additional releases of these compounds into the environment through effluent, sludge or via paper products.

Small amounts of TCDD and TCDF can be formed, along with many other chlorinated organic chemicals, when wood pulp is bleached with chlorine gas.

About 10 percent of the total solids in the waste streams of bleaching plants contain chlorinated derivatives, but this varies among mills depending on the degree of filtration. Some European countries, Sweden and the Federal Republic of Germany in particular, have imposed restrictions on the amount of total organically bound chlorine (TOCl) that they will allow their pulp and paper industry to discharge.[5] Sweden has cut the amount of allowable TOCl discharge more than half, from the 5 to 6 kilograms per metric ton (kg/t) of pulp normally produced with conventional chlorine bleaching, to 2 kg/t. Oxygen delignification and chlorine dioxide substitution have been the technology of choice to meet Sweden's environmental requirements. The National Swedish Environmental Protection Board hopes to reduce TOCl to 0.1 kg/t by 2010 and to 1.5 kg/t by 1992. With further reductions in allowable discharges, the Swedish industry may need to adopt closed-cycle processes to eliminate chlorinated discharges entirely.

Sweden and the Federal Republic of Germany have moved from regulating pulp mill discharges by limits on chemical oxygen demand, to limits on the amount of total organic chlorine released per ton of pulp produced. This will have a forcing

[5]Between 250 and 300 chemicals have been identified in pulp mill effluents. Many of them are chlorinated organic compounds. See Leena R. Suntio, Wan Ying Shiu, and Donald Mackay, "A Review of the Nature and Properties of Chemicals Present in Pulp Mill Effluents," *Chemosphere*, vol.17, No. 7, 1988, pp. 1249-1290. TCDD and TCDF make up a very small fraction of the total organochlorine emissions.

effect on the pulping, bleaching, and waste treatment technologies used in those countries.

In 1988 the Board also considered the overall problem of dioxin in the Swedish environment and concluded that standards established for reducing TOCl would suffice to reduce the dioxin levels from bleached pulp as well. Chlorinated organic effluents from pulp and paper manufacture have created environmental problems in coastal waters and estuaries of the Baltic Sea, particularly in the enclosed Gulf of Bothnia. Unlike U.S. pulp mills that use secondary biological sewage treatment technologies to treat waste effluents, mills in Sweden, some in Finland, and many in Canada do not use comparable treatment methods before discharging into the environment. Biological treatment can remove large amounts of chlorinated contaminants (particularly those that adhere tightly to sediments such as TCDD and TCDF) from mill effluents when operated properly. Biological treatment transfers the contaminants from the water and concentrates it in the sludge. The sludge must then be disposed of in a safe and acceptable manner. Biological treatment systems require constant attention to ensure that they are working efficiently.

U.S. environmental regulations that limited the release of "conventional" pollutants from pulp mills induced the domestic industry to install secondary biological waste treatment plants to meet the standards. Most plants in Europe and many in Canada do not have secondary waste treatment.

The Federal Republic of Germany will begin tightening restrictions on the discharge of chlorinated organics in 1989. Maximum allowed discharges of organochlorines will be 1.0 kg/t of bleached pulp under the new regulations. Until recently, West German regulations for pulp mill discharges have not been overly strict. Fees levied on discharged amounts of oxygen demand, solids, and measures of toxicity to fish have allowed the German industry to "buy" the right to pollute.

Chlorinated organic residues from pulp bleaching have caused less concern in North America where little research into adverse impacts on fisheries and aquatic biota has been conducted. There is ample experimental evidence, however, that pulp mill effluents, unless adequately treated, can be toxic to fish and some chlorinated compounds may ultimately find their way through the food web. Dioxin has been shown to be extremely toxic to fish at very low concentrations under controlled laboratory experiments and has been linked to periodic reductions in reproductive rates of some bird species. U.S. mills, unlike their European counterparts, have installed extensive biological treatment systems to reduce the biological and chemical oxygen demand (BOD and COD) of their waste effluents before discharging them into streams. U.S. environmental requirements for the issuance of a discharge permit for conventional pollutants, such as BOD, COD, and suspended solids, and toxicity tests on mill effluents make biological waste treatment a preferred technology for U.S. mills.

Dioxin levels in some whole fish sampled in the National Dioxin Study and in other samples taken below pulp mills exceeded the safe levels prescribed by the FDA. It is known that fish can accumulate dioxins in their bodies (concentrating mostly in the inedible body parts) many thousands of times more than the concentrations of dioxin in the receiving waters. Ingestion by eating contaminated fish may be the source of the public's greatest exposure to dioxin resulting from pulp manufacture.

The detection of dioxin in some fish samples reported in EPA's National Dioxin Study has

raised concern about the possible effects on human health. Less than 20 percent of the *randomly* selected sites sampled by EPA in the study showed detectable quantities (more than one part per trillion [ppt]) in whole fish samples. Other samples collected at over 300 *regional* sites selected by EPA for high probability of dioxin contamination showed that nearly one-third of the rivers, lakes, coastal waters, and estuaries contained fish with detectable amounts of dioxin that ranged up to 85 ppt—significantly higher than the 25 ppt determined to be unsafe by the Food and Drug Administration (contained in edible fillets, not in whole fish)—but it is not certain that pulp mill waste was the source of all contamination. Only 4 of 57 *estuarine and coastal* sites sampled in the National Dioxin Study had detectable levels of dioxin in fin fish or shellfish. Based on laboratory tests, fish have been shown to accumulate dioxin in their bodies at rates approximately 20,000 to 85,000 times the concentrations to which they are exposed in water. Fishing has been prohibited in several rivers because of dioxin levels, and advisories have been issued by Wisconsin, Maine, and Louisiana warning of the possible risks of eating contaminated fish.

A screening analysis of pulp waste at five bleached kraft pulp mills, which was conducted jointly by EPA and the U.S. paper industry, and other research in Europe and Canada clearly links the formation of TCDD and TCDF to the chlorine bleaching process. TCDD was detected in seven of nine bleached pulps sampled, some with levels as high as 51 ppt. TCDF, which is less toxic than TCDD, was found in eight of nine pulps sampled, with levels ranging up to 330 ppt.

Dioxin was detected in wastewater at four of the five mills, but concentrations varied greatly among the mills sampled. The highest levels of TCDD and TCDF were associated with waste from the caustic extraction stage, which is designed to remove the dissolved materials after the chlorine treatment. EPA and the paper industry are currently surveying 104 additional mills to better determine the scope and extent of dioxin and furan formation. Detailed analyses of TCDD levels and bleaching processes at 25 pulp mill bleach lines will be conducted in the course of the study.

Based on information available to date, it is not clear whether, by themselves, residual TCDD or TCDF in pulp and paper products present significant health risks to the public. Potential exposure from paper products should not be considered trivial, however. Recent test results showing higher than expected migration rates of dioxin from paper milk cartons into milk indicate that further tests of food packaging and products linked to the possible ingestion of dioxin is warranted. Compared to other common sources of daily ambient exposure to dioxin, dermal exposure from paper products seems to be comparatively small. Estimates of the cumulative exposure from multiple sources must be considered. An Interagency Task Force led by EPA is currently attempting to do this.

The detection of TCDD and TCDF in bleached pulp samples raised concern about whether residual dioxin was being carried forward into finished paper products. The National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), the industry's environmental research arm, commissioned an assessment of the potential risks to human health from skin exposure to a variety of paper products, including disposable diapers, facial tissue, toilet tissue, sanitary napkins, coffee filters, and paper towels. The assessment concluded that TCDD equivalents in all products tested presented a lifetime cancer risk of less than one in a million.

Environmentalists note that NCASI's assessment only considered the risks for 2,3,7,8-TCDD and 2,3,7,8-TCDF without examining

the risks from the several hundred other chlorinated byproducts that are also found in paper products, and that NCASI failed to consider the cumulative risk of using a wide range of paper products daily. Environmentalists also fault NCASI for not using appropriate testing procedures for evaluating the possible enhanced mobility of dioxin when in the presence of lipids, solvents, and fats, such as encountered when using paper towels for cooking or when using creams and baby oils with disposable diapers.

OTA learned at its dioxin workshop that there is considerable disagreement about the validity of the testing protocols for determining the rate of migration of dioxin from paper products and into the human body. For instance, there are widely differing opinions about how to estimate the effect of urine leaching from disposable diapers into the skin of babies, and how to simulate the environment of a tampon in determining the movement of dioxin into a woman's body. Without standard protocols, disagreements over the meaning of dioxin risk data leaves OTA with no means to evaluate the industry's findings and conclusions. Evaluation of these testing techniques is beyond the scope of this assessment.

Agreement is also lacking on how to express levels of risk. Does one accept a one in a million risk of cancer as did the U.S. paper industry in its study of risks from dermal exposure to dioxins, or should the acceptable risk be one in a thousand? There are *no* Federal regulatory standards. Arbitrary levels of risk are used for convenience, and experts differ over the most appropriate levels to use.

Semantics also contribute to the confusion: Should dioxin exposure levels be expressed as "virtually safe dose," which implies that there "is a level of exposure at which the cancer risk is zero," or should the term "risk specific dose" be used since it does not imply that there is any dose above zero that is "safe"?

Couple the uncertainties over testing protocols with disagreement over levels of acceptable risk, and add to it the lack of consensus about the potency of dioxin to humans, and a confused picture is presented to those attempting to gauge the danger of dioxin from pulp manufacture and paper use.

OTA is aware of no published studies that have attempted to define worker exposures to dioxin in paper mills using environmental measurements or biological exposure measurements, such as serum or fat TCDD/TCDF concentrations. The National Institute of Occupational Safety and Health (NIOSH), the Federal agency charged with occupational and health research, is currently developing personal exposure monitoring methods to address pulp and paper workers' exposure to dioxin.

EPA is currently coordinating an Interagency Task Force on Dioxin in Paper aimed at gauging the cumulative risk of all of the media that could contribute to human exposure. Other cooperating agencies include the Food and Drug Administration and the Consumer Product Safety Commission (CPSC). The interagency effort was characterized by an EPA official at the November 1988 OTA dioxin workshop as an effort to "determine whether there is a risk—not a 'gold plated' risk assessment," and a "snapshot in time" as to the risk aimed at determining whether regulation is needed. The interagency study will build on both the EPA/Industry 104-mill study and estimates of migration rates of dioxin from paper products. It will include an assessment, based on product-use scenarios, of technologies that could reduce dioxin exposure.

OTA found that, as with many other Federal activities, the analytical and regulatory authority for dealing with dioxin in paper is fragmented among several agencies, none of which have clear responsibility for dealing with the problem in its entirety. While EPA has jurisdiction over water pollution and dioxin in pulp (dealt with in two separate offices), FDA has responsibility

for regulating dioxins in coffee filters and sanitary napkins, and CPSC has responsibility for dioxin in disposable diapers, paper towels, facial tissues, and toilet tissues.

The lack of published independent Federal research on the risks associated with dioxin in paper products and the absence of government information on paper worker's environmental exposure to dioxin required OTA to rely almost wholly on industry-sponsored research. The paucity of government information on workers' risk and exposure to dioxin in paper products may change in the future as a result of the Interagency Task Force on Dioxin in Paper mentioned above, but in the meantime we have only industry information available to evaluate the potential risks from dioxin in paper.

Pulp Bleaching Technology

About 10 percent of the lignin found originally in wood is carried over from the chemical digestion process to the bleaching stages in kraft mills. This residual lignin must be substantially reduced if pure cellulose products or bright paper are to be produced. The less lignin retained in the pulp as it leaves the digester, the less bleaching needed. There are limits, however, as to how much digestion wood fibers can endure without sacrificing pulp strength and paper durability or significantly reducing pulp yield.

The tendency has been to bleach more pulp as the demand for products using bleached paper increases. Most of the bleached pulp has been produced by the kraft chemical process. Very little mechanical pulp has been bleached in the past, but now it is increasing at twice the rate of chemical pulp bleaching worldwide. Mechanical pulp is not normally bleached with chlorine gas but with hydrogen peroxide or sodium hydrosulfide.

Bleaching is a continuation of the delignification process and is used to brighten and purify the wood pulp. The purer the cellulose and brighter the paper, the less lignin retained, and the longer the paper will last without yellowing and becoming brittle. Chlorine gas has become the preferred bleaching agent because of its relatively low cost and high effectiveness. However, a number of other bleaching chemicals are also used, including hypochlorite, chlorine dioxide, oxygen, and hydrogen peroxide. Ozone has also been tried under experimental conditions, but is not yet commercially available. Each has its advantages and disadvantages, and several are usually used in sequence to achieve the final result. Between bleaching stages caustic chemicals are often used to remove the dissolved lignin and wash the fibers before they are subjected to additional bleaching. It is apparently during this extraction that much of the dioxin created by chlorine bleaching finds its way into the waste stream.

By reducing or eliminating the use of chlorine gas in the bleaching process, the amount of chlorinated organic waste products and dioxin can be reduced. The reduction or elimination of organic precursors that form dioxin can also reduce the amount of dioxin produced. Little is currently known about these precursors—although knowledge is accumulating rapidly—and more research is needed in this area.

It has been shown that by reducing the use of chlorine gas in the bleaching process, the amount of chlorinated organic residues and contaminates can be reduced. Oxygen delignification shows some promise for reducing the amount of lignin carried with the pulp to the bleach process, thus reducing the amount of chlorine gas needed to bleach the pulp to the desired brightness. Current commercial oxygen delignification technology can reduce the use of chlorine gas by 40 to 50 percent. Further

reductions in the use of chlorine by more intense oxygen delignification is limited by severe losses in pulp yield and strength properties. Pretreatment of the pulp with nitrogen dioxide before oxygen treatment shows promise for increased delignification before bleaching.

The cost advantage that chlorine gas once had over many other bleaching agents does not apply to oxygen. If the U.S. pulp and paper industry is required to reduce the amount of chlorinated organics and dioxin produced in bleaching pulp, oxygen may become a partial substitute for chlorine because of its low operating cost. Capital cost for oxygen treatment is very high, however, and installation of oxygen delignification in existing mills can reduce production capacity as much as 4 or 5 percent. Any evaluation of the comparative costs of oxygen technology with other delignification systems should consider both capital costs, life-cycle costs based on operating costs and depreciation, and gains and losses in productivity and quality. Such analyses were not made by OTA in this study.

Technologies for Reducing Dioxin

There are several ways to reduce the amount of pollution contributed by bleach plants. These include:

- further delignification of pulp before bleaching;
- improved washing of the unbleached pulp (brownstock);
- substitute nonchlorinated bleach agents;
- substitute chlorine dioxide for some or all chlorine gas;
- apply multiple additions of chlorine in split charges instead of using a single, massive charge (low chlorine multiple);
- improve chemical mixing with the pulp;
- adjust the acidity of the unbleached stock before adding chlorine;
- use "cleaner" oil-base defoamers that do not contain dioxin precursors;
- remove dioxin precursors prior to treatment of the pulp with chlorine; and
- improve secondary waste treatment and waste-disposal practices.

Pretreatment before bleaching can reduce the amount of chlorine or other bleaching chemical used. Technologies for prebleach delignification include: 1) extended delignification, 2) oxygen delignification, 3) pretreatment with nitrogen dioxide before oxygen delignification (PRENOX allows more lignin to be removed without damaging fibers), 4) pretreatment with other chemicals such as chlorine dioxide, and 5) extraction with sodium hydroxide supplemented with oxygen and hydrogen peroxide. Only extended delignification and oxygen delignification are currently used commercially.

Other technologies used to conserve water and reduce energy consumption may also help reduce the amount of chlorinated products in the waste stream:

- recycle process water from the chlorination stage (although this may actually compound the dioxin problem),
- use countercurrent washing systems after chlorination, and
- reduce water use by using higher ratios of fiber pulp to water (higher consistency).

Elimination of chlorine in the bleach sequence combined with internal recycling of process water aimed at developing a "pollution-free" pulping system seems to offer a good strategy over the long term, but has not yet been adopted for commercial use.

There are several possible ways to reduce the use of chlorine gas in bleaching to high pulp brightness: 1) substitute chlorine dioxide for part or all of the chlorine, 2) use hydrogen peroxide or ozone (experimental only), and 3) extraction between bleach stages with sodium hydroxide, supplemented with oxygen and hydrogen peroxide.

It is believed that if the use of chlorine gas is reduced or eliminated in the bleaching process, the amount of TCDD and TCDF formed will be lowered or eliminated along with other chlorinated organics. However, the relationship is not linear, and other factors, such as mixing efficiency, have significant effects on the relationship. Oxygen is one of the most promising bleaching chemicals for displacing some of the chlorine used in the bleaching cycle. In no case thus far has oxygen been able to completely eliminate the need for chlorine.

Chlorine dioxide, a more efficient oxidant than chlorine, can be substituted for substantial amounts of chlorine gas. The use of chlorine dioxide in conjunction with chlorine gas is increasing at U.S. mills. It has been demonstrated that substitution of chlorine dioxide for some optimum portion of chlorine gas can significantly reduce the formation of TCDD and TCDF. However, the effects of chlorine dioxide substitution on the formation of other chlorinated compounds are not known.

It may also be possible to reduce the amount of TCDD and TCDF formed by chlorine bleaching if the acidity (pH) of the reaction is controlled closely and/or if the chlorine is applied in smaller, multiple charges instead of one large charge. Further experimentation is needed to verify the potential of these process modifications.

Recent research has also shown that the amount of dioxin can be reduced by lowering the acidity (raising the pH) of the pulp before chlorination, by applying the chlorine charge in three parts instead of one shot, and by using chlorine dioxide after an initial charge of chlorine gas. A very recent discovery by scientists at the Pulp and Paper Institute of Canada has identified oil-based defoamers as one possible source of the precursors that form dioxin when chlorinated. As a consequence, the U.S. industry and chemical suppliers are currently seeking cleaner oil-based defoamers.

Precursors must be present for TCDD and TCDF to be formed by reaction with chlorine. There are a number of possible sources: 1) natural constituents in the wood, 2) contaminants in the pipes and machinery of the pulp mill, and 3) additives—chemicals added to the pulp to improve the pulping and bleaching processes. Some defoamers added to the pulp may be contaminated with precursors that can form dioxin when chlorinated. Chemical suppliers and the pulp and paper industry are searching for clean defoamers, but none are currently available that can be used effectively for brownstock washing.

Defoamers are added to the unbleached pulp in small amounts to improve washing. If a defoamer is made from used oil contaminated with unchlorinated dioxins (DBD) and furans (DBF), these precursors convert to their chlorinated forms as TCDD and TCDF when exposed to chlorine gas. The United States regulates the use of contaminated recycled oil, so further investigation is needed to determine whether defoamers are a problem for U.S. mills using domestically produced products. Recent investigations by American scientists using testing protocols more sensitive than those used in Canada have raised doubts as to whether any oil-based defoamers—whether made from ei-

ther virgin, hydro-treated oil, or used oil—are free of contaminating precursors.

Water-based defoamers are also available, and tests show them to be free of DBD and DBF precursors. Unfortunately, while water-based defoamers can be used at other washing stages in the mill, they are not effective for washing brownstock. The use of "cleaner" defoamers is another option for reducing some of the dioxin produced in the bleaching process, but more research and development may be needed to develop suitable products.

Oxygen delignification technology was discovered in 1952, and the first commercial unit was installed in the 1960s. Since then, oxygen technology has advanced steadily until it is now considered a mature and proven process. In 1988, world installed capacity using oxygen delignification is expected to exceed 10 million metric tons per year. Several manufacturers of pulp and paper equipment market oxygen delignification systems. Over 50 oxygen units have been installed worldwide. About half the oxygen capacity is in Scandinavia and Europe, one-fifth is in Japan, and one-fifth is in North America. About 92 percent of the oxygen bleaching capacity is installed in kraft mills, but a number of sulfite mills—mostly in the Federal Republic of Germany—have also installed oxygen delignification units.

Oxygen can also be used in combination with extended digestion (modified cooking). By modifying the chemical addition and allowing it to cook longer, the amount of residual lignin in the pulp can be reduced prior to bleaching. Further pre-bleaching with oxygen can produce pulp with even lower amounts of lignin. With pre-bleached pulps of low lignin content, it may be technically possible to eliminate the use of chlorine gas in the bleaching process if chlorine dioxide is used as a substitute.

No reliable data exist that *directly* link the reduction of TCDD and TCDF wholly to oxygen delignification, and in some cases oxygen pulps have been shown to contain some TCDD and TCDF. There is, however, substantial evidence that oxygen delignification after pulping and before the first bleaching stage *can reduce* the amount of chlorinated organics produced in proportion to the reduction in residual lignin. At this time, too few comparative analyses have been made of dioxin in oxygen-treated pulps v. that in conventional pulp to absolutely support the hypothesis that oxygen bleaching substantially reduces TCDD and TCDF in bleached pulps, although unpublished EPA data based on three mills sampled in 1988 seem to support this hypothesis.

There is no "silver bullet" for reducing the TCDD and TCDF in bleached pulp. Several technologies and/or process modifications may be used individually or in combination. The choice of technologies and their effectiveness depends on the existing mill configuration and the quality of the pulp produced. New mills have more flexibility.

Modern mills are designed to match the capacity of the chemical recovery plant with the planned production capacity of the mill. The addition of an oxygen delignification stage increases the volume of effluent that must be handled by the chemical recovery plant. In new mills recovery plants can be designed to handle the additional load, but retrofitting an existing mill with an oxygen delignification system can result in overloading the chemical recovery capacity. If a larger size recovery furnace or evaporators are required, the additional capital expense may make oxygen delignification a less attractive alternative for economic reasons. It is estimated that adding an oxygen stage to a mill whose chemical recovery plant is operating at full capacity will reduce the productivity of that mill 4 to 5 percent.

Given a range of equally effective technologies to reduce the use of chlorine gas, capital and

operating costs may determine the most cost-effective strategy for reducing the amount of chlorinated organic chemicals produced by pulp mills. Although operating costs may be lower if oxygen delignification is used to replace some of the chlorine gas now used in the bleach cycle, the capital cost of oxygen systems is large. Both capital costs and operating costs must be considered in a balanced assessment. Furthermore, cost factors will differ from mill-to-mill, making generalizations difficult. OTA did not attempt to assess these costs. On the other hand, by using "cleaner" defoamers, coupled with substitution of chlorine dioxide for chlorine, it may be possible to achieve much lower levels of TCDD and TCDF in pulp. Whether or not this would also lower the level of other chlorinated compounds is uncertain.

Additional control of suspended solids that bind TCDD and TCDF by adding clarifiers or sorbents to the biological waste treatment systems, and/or dechlorination of bleach plant waste might prove effective in removing dioxin from effluent at some mills. Dioxin-bearing sludge must then be disposed of in a safe and appropriate manner.

Further reductions in environmental releases from pulp mill waste outfalls may result from improving the control of suspended solids in the secondary waste treatment plant. TCDD and TCDF are relatively insoluble in water, but they adhere tightly to fine colloidal material and suspended solids. A well-designed, properly operated secondary treatment plant is capable of removing up to 90 percent of the TCDD and TCDF released. Dioxins are retained in treatment plant sludge. The sludge is normally disposed of in landfills, where limited studies show that it remains isolated and immobile. Some sludge is retained in sludge lagoons or is incinerated, but a portion is used for soil conditioners. The remaining 10 percent of the dioxin that remains in suspension can find its way in to the water coarse and remain as sediment in streambeds. The use of clarifiers, chemicals, and settling basins to improve the efficiency of waste treatment, coupled with chlorine dioxide substitution and/or perhaps other delignification technology might prove to be the optimum solution for some existing pulp mills.

More questions remain than do answers as to what risk dioxin from pulp and paper manufacture presents to humans and the environment: will additional regulations be needed to reduce the risk of human exposure from dioxin and other chlorinated compounds produced in pulp mills? and which technologies or mix of technologies are best suited for reducing the production of dioxin in the pulp bleaching process? The pulp and paper industry has a number of technical options available to meet the problem. Other technologies, such as extended delignification and the substitution of other oxidants in the bleach process for chlorine gas, may be as effective as oxygen delignification in reducing the use of chlorine. All of these questions require more detailed study before they can be answered with acceptable certainty. Final decisions to meet regulatory requirements will have to be made on a case-by-case, mill-by-mill basis.

Chapter 2

The Pulp and Paper Making Processes

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Chapter 2

The Pulp and Paper Making Processes

The modern manufacture of paper evolved from an ancient art first developed in China, ca. 105 A.D. Although the modern product differs considerably from its ancestral materials, papermaking retains distinct similarities to the processes developed by Ts'ai Lun in the Imperial Chinese Court.[1] In principle, paper is made by: 1) pulping, to separate and clean the fibers; 2) beating and refining the fibers; 3) diluting, to form a thin fiber slurry, suspended in solution; 4) forming a web of fibers on a thin screen; 5) pressing the web to increase the density of the material; 6) drying to remove the remaining moisture; and 7) finishing, to provide a suitable surface for the intended end use.

Pulp and paper are made from cellulosic fibers (i.e., fibers from trees) and other plant materials, although some synthetic materials may be used to impart special qualities to the finished product. Most paper is made from wood fibers, but rags, flax, cotton linters, and bagasse (sugar cane residues) are also used in some papers. Used paper is also recycled, and after purifying and sometimes deinking, it is often blended with virgin fibers and reformed again into paper. Other products made from wood pulp (cellulose) include diapers, rayon, cellulose acetate, and cellulose esters, which are used for cloth, packaging films, and explosives.

Wood is composed of: 1) cellulose, 2) lignin, 3) hemicellulose, and 4) extractives (e.g., resins, fats, pectins, etc.). Cellulose, the fibers of primary interest in papermaking, comprises about 50 percent of wood by ovendry weight. Lignin, which cements the wood fibers together, is a complex organic chemical the structure and properties of which are not fully understood. It is largely burned for the generation of energy used in pulp and paper mills. As the chemistry of lignin becomes better understood, what is now mostly a waste product used for fuel (some is converted to chemical products) could become a valuable feed stock for new chemical products.

The pulping process is aimed at removing as much lignin as possible without sacrificing fiber strength, thereby freeing the fibers and removing impurities that cause discoloration and possible future disintegration of the paper. Hemicellulose is similar to cellulose in composition and function. It plays an important role in fiber-to-fiber bonding in papermaking. Several extractives (e.g., oleoresins and waxes) are contained in wood but do not contribute to its strength properties; these too are removed during the pulping process.

The fiber from nearly any plant or tree can be used for paper. However, the strength and quality of fiber, and other factors that can complicate the pulping process, varies among tree species. In general, the softwoods (e.g., pines, firs, and spruces) yield long and strong fibers that impart strength to paper and are used for boxes and packaging. Hardwoods, on the other hand, generally have shorter fibers and therefore produce a weaker paper, but one that is smoother, more opaque, and better suited for printing. Both softwoods and hardwoods are used for papermaking and are sometimes mixed to provide both strength and printability to the finished product.

THE PULP AND PAPER MILL

Although there are several chemical and mechanical pulping methods used for delignifying wood (table 2-1), separating fibers, and removing discoloration, all integrated pulp and paper mills involve the same general steps in the manufacture of pulp and paper. These steps include: 1) raw material preparation (e.g., debarking and chipping); 2) mechanical and/or chemical separation of the wood fibers [i.e., grinding, refining, or digestion (cooking)] to dissolve the lignin and extractives; 3) removal of coloring agents (primarily residual lignin) by bleaching; and 4) paper formation and manufacture.

A typical layout of a mill using the kraft chemical pulping process is shown in figure 2-1. Mechanical, semichemical, and sulfite pulp mills differ in detail, particularly in wood preparation, fiber separation, and bleaching, but many of the downstream refining, bleaching, and papermaking processes are similar. In addition to the primary steps in pulp and paper manufacture, each mill has extensive facilities to

[1]A.H. Nissan, *Paper, Wood: Its Structure and Properties*, F.F. Wangaard (ed.) (University Park, PA: Pennsylvania State University 1981), p. 335.

Table 2-1—Major Commercial Wood-Pulping Technologies

Pulp grades use	Wood type	End-product use
Chemical pulps:		
Sulfite pulp	Softwoods and hardwoods	Fine and printing papers
Kraft sulfate pulp	Softwoods and hardwoods	Bleached—printing and writing papers, paperboard
		Unbleached—heavy packaging papers, paperboard
Dissolving pulp	Softwoods and hardwoods	Viscose rayon, cellophane, acetate fibers, and film
Semichemical pulps:		
Cold-caustic process	Softwoods and hardwoods	Newsprint and groundwood printing papers
Neutral sulfite process	Hardwoods	Newsprint and groundwood printing papers
Mechanical pulps:		
Stone groundwood	Softwoods	Corrugating medium
Refiner mechanical (RMP)	Softwoods	Newsprint and groundwood printing papers
Thermomechanical (TMP)	Softwoods	Newsprint and groundwood printing papers

SOURCE: Modified from George H. Boyd III and Chad E. Brown, *Paper Industry: Outlook for Market Pulp* (New York, NY: Kidder, Peabody & Co., 1981), p. 5.

produce and reclaim chemical agents used in the pulping process; collect, process, and burn lignin and waste wood to produce energy; and remove and treat wastes from process water for release into the environment.

Steps in the Pulp and Papermaking Process

Raw Material Preparation

Wood received at a pulp mill may be in several different forms, depending on the pulping process and the origin of the raw material. It may be received as bolts (short logs) of roundwood with the bark still attached, as chips about the size of a half-dollar that may have been produced from sawmill or veneer mill waste or pre-chipped from debarked roundwood elsewhere, or as waste sawdust in the case of some pulping processes.

If roundwood is used, it is first debarked, usually by tumbling in large steel drums where wash water may be applied. The debarked wood bolts are then chipped in a chipper if the pulping process calls for chemical digestion or are fed into a grinder in the case of some mechanical pulps. Chips are screened for size, cleaned, and temporarily stored for further processing.

Fiber Separation

The fiber separation stage is the point at which the several pulping technologies diverge. In kraft chemical pulping, the chips are fed into a large pressure cooker (digester), into which is added the appropriate chemicals (white liquor). The chips are then cooked (digested) with steam at specific temperatures long enough to separate the fibers and partially dissolve the lignin and other extractives.

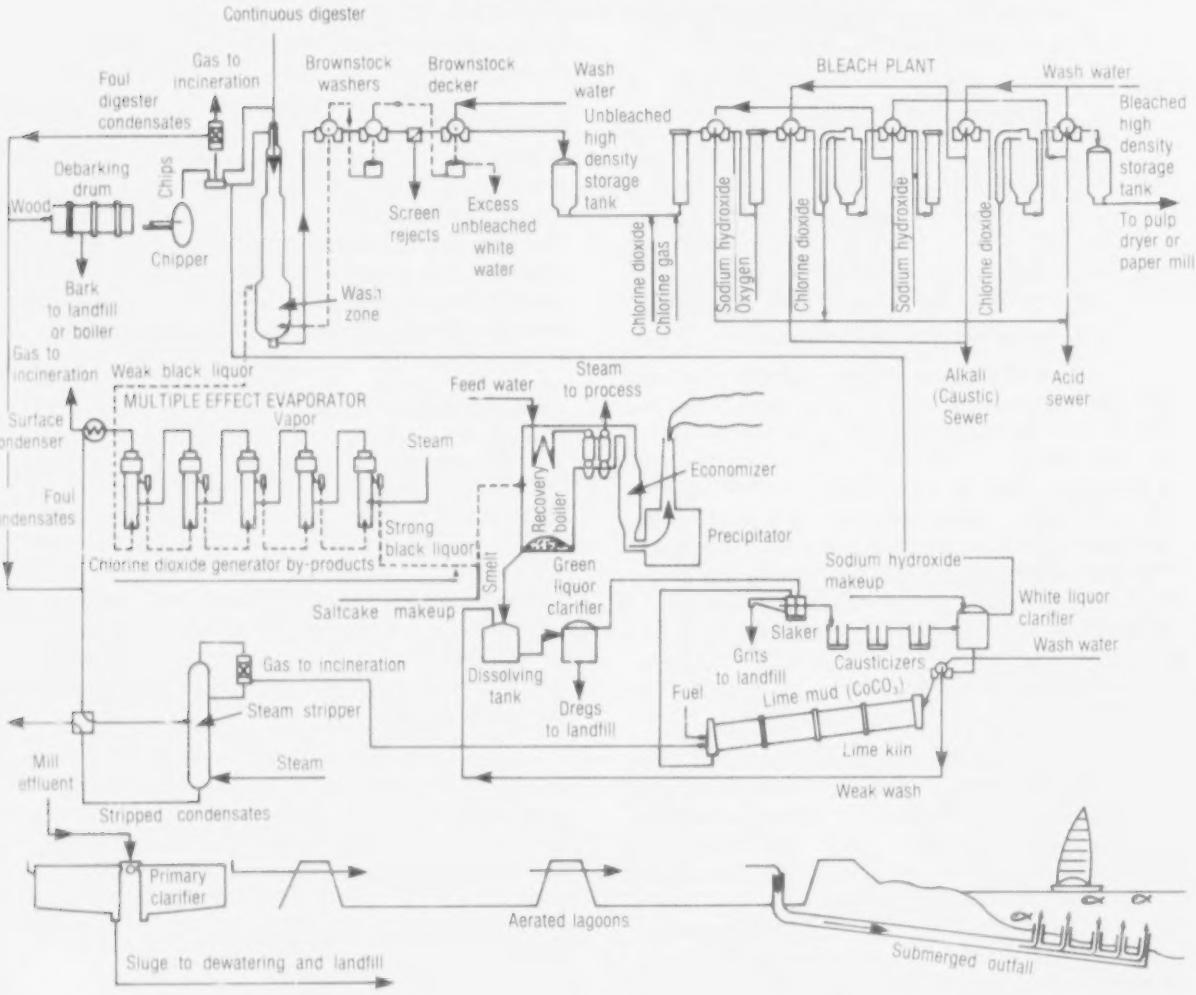
Some digesters operate continuously with a constant feed of chips (furnish) and liquor, others are charged intermittently and treat a batch at a time. After digestion, the cooked pulp (brown stock) is discharged into a pressure vessel (blow tank) where the steam and volatile materials are siphoned off. The cooking liquor, that by this time has turned dark brown from the dissolved lignin (black liquor), is returned to the chemical recovery cycle. In the chemical recovery plant, the lignin in the black liquor is burned for the cogeneration of energy, and the chemicals are recovered, purified, reconstituted, and returned to the digester as white liquor for reuse.

The brown stock containing the recovered fibers (having the consistency of cooked oatmeal) is washed with water, screened to remove undigested wood, and cleaned to remove other foreign matter. It is then ready for bleaching and further processing.

Fiber separation in mechanical pulping is less dramatic. In the stone groundwood process, debarked logs are forced against rotating stone grinding wheels that are constantly washed by a stream of water. The ground pulp is then screened to remove course debris, thickened, and stored for the papermaking process.

Chips are used to produce refiner puip and thermomechanical pulp. In both processes the chips are ground by passing them through rapidly rotating

Figure 2-1—Overall View of Papermaking From Chemical Pulp by the Kraft Process



SOURCE: Environment Ontario, *Stopping Water Pollution At Its Source* (Toronto, Ontario: Ministry of the Environment, 1988).

disk grinders. Thermomechanical pulp is refined (ground) under pressure after the chips are pretreated with steam (chemical thermomechanical pulp uses chemicals and steam for pretreatment). After further refining in a second stage, the pulp is screened, cleaned, and most of the process water is removed in preparation for papermaking.

Bleaching or Brightening

Since the raw pulp (brown stock) still contains an appreciable amount of lignin and other discoloration, it must be bleached to produce light colored or white papers preferred for many products. Bleaching is normally done in several stages (multistage bleaching). Through chlorination and oxidation the fibers are further "delignified" by solubilizing additional lignin from the cellulose.

A number of bleaching agents may be used and are applied in a stepwise fashion within a bleaching sequence. These include chlorine gas, chlorine dioxide, sodium hypochlorite, hydrogen peroxide, and oxygen. Between bleaching treatments, a strong alkali (usually sodium hydroxide) is used to extract the dissolved lignin from the surface of the fibers. The bleaching agents and the sequence in which they are used depend on a number of factors, such as the relative cost of the bleaching chemicals, type and condition of the pulp, desired brightness of the paper to be produced, and sometimes in response to environmental guidelines and regulations.

Bleaching of mechanical pulp is much different than that for chemical pulp. Mechanical pulping leaves the lignin and the cellulose intact, whereas the purpose of chemical pulping is to chemically separate the lignin from the cellulose fibers and remove it from the pulp. A major advantage of mechanical pulping is the high yields of pulp that can be achieved from a given volume of wood. Therefore, bleaching or brightening of mechanical pulps is designed to minimize the removal of the lignin that would reduce fiber yields.

Chemicals used for bleaching mechanical pulps selectively destroy coloring impurities but leave the lignin and cellulosic materials intact. These include sodium bisulfite, sodium or zinc hydrosulfite (no longer used in the United States), calcium or sodium hypochlorite, hydrogen or sodium peroxide, and the Sulfur Dioxide-Borol Process (a variation of the sodium hydrosulfite method). Originally, much of the mechanical pulp was not bleached, but the bleaching of groundwood has increased and improved technology now enables bleached groundwood pulp to be used for printing papers, tissues, and towelling.

Papermaking

The bleached or unbleached pulp may be further beaten and refined to cut the fibers and roughen the surface of the fibers (fibrillate) to improve formation and bonding of the fibers as they enter the paper machine. Before entering the paper machine, water is added to the pulp slurry to make a thin mixture normally containing less than 1 percent fiber. The dilute slurry is then cleaned in cyclone cleaners and screened in centrifugal screens before being fed into the "wet end" of the paper-forming machine.

In the paper making process, the dilute stock passes through a headbox that distributes the fiber slurry uniformly over the width of the paper sheet to be formed. The "web" of fiber that will make the new paper sheet is formed on a continuously moving bronze or polymer screen (Fourdrinier) or between two such wire screens. Water drains from the slurry through the mesh of the screen, the wet paper web is consolidated and the paper sheet gains some strength through fiber bonding.

The wet sheet of paper is continuously lifted from the screen (couched) and transferred to a woven felt belt where additional water is squeezed from the paper sheet by pressure rollers. The remaining water is removed on steam-heated cylinders. When the paper is dry it may be treated with stabilizing materials and surface finishes to improve durability or printability.

Pulping Technologies

Mechanical Pulping Processes

There are six basic mechanical pulping processes: 1) stone groundwood, 2) refiner, 3) thermomechanical pulping, 4) chemical mechanical, 5) defibrated or exploded pulping, and 6) recycled paper.[2] Mechanical pulping is generally used with softwoods be-

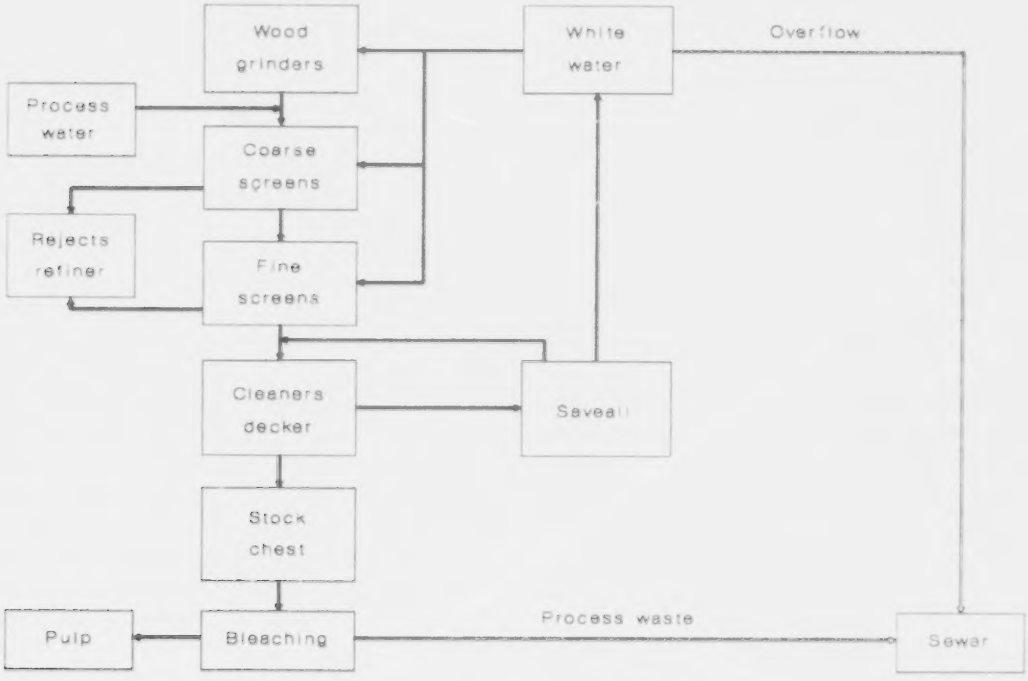
[2]This section on pulping technologies borrows heavily from a previous OTA assessment: *Wood Use: U.S. Competitiveness and Technology, Vol. II Technical Report*, OTA-M-224 (Springfield, VA: National Technical Information Service, 1984), pp. 79-94.

cause of the added strength imparted by the long fiber length of softwood species. Some hardwoods require chemical pretreatment (chemical mechancial pulping) to produce a suitable groundwood pulp. Fibers separated mechanically are substantially damaged in the process and therefore make weaker paper or paperboard. However, since both lignin and cellulose fibers remain intact, the yield of paper per unit volume of wood is still greater than that produced by chemical pulping. Pulp yields from all of the mechanical pulping processes typically are near 90 to 95 percent recovery, which is a much higher yield per unit of wood than with the chemical pulping methods because of the retention of lignin. However, paper made from mechanical pulp discolors and becomes brittle with age because of its lignin content, which results in a shorter useful life than paper made from chemical pulp.

Mechanical pulps are used principally to manufacture newsprint, printing papers, towelling, tissue, and coated specialty papers that do not require high-strength. Secondary uses include wallpaper and paperboard. Small amounts of chemical pulp are often mixed with groundwood pulp for additional strength. Recycled pulp is used mainly for the manufacture of folding boxboard (grayboard), tissue, corrugated board, and newsprint. Paper products made from defibrated pulp include hardboards, construction boards, and roofing papers.

In the stone groundwood process, debarked short logs (roundwood) are fed whole against wet stone grinders by hydraulic rams. Counter-revolving steel disks are sometimes used in place of abrasive stone in the grinding process. The abrasion of the grinding wheel against the wood physically separates the wood fibers. The grinding process usually is automatic and continuous. The groundwood pulp is then screened, bleached or brightened, treated, and prepared for the paper machine (figure 2-2).

Figure 2-2—Stone Groundwood Pulp Mill Flow



SOURCE: Allan M. Springer, *Industrial Environmental Control: Pulp and Paper Industry* (New York, NY: John Wiley & Sons, 1986), p. 147.

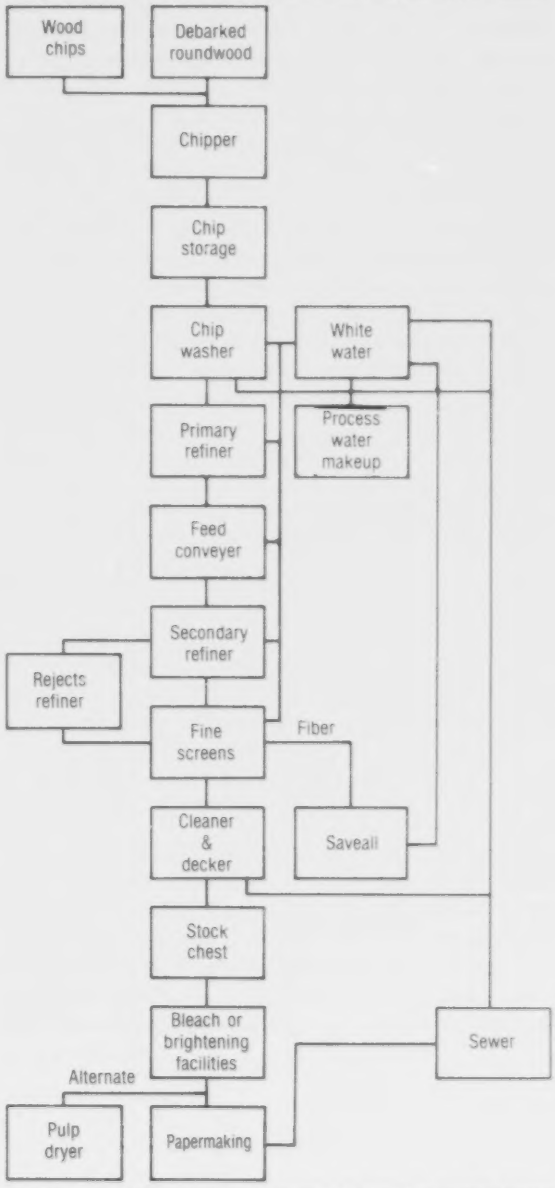
Refiner mechanical pulping (RMP) uses chips in lieu of roundwood and produces paper with higher strength than conventional groundwood because of less damage to the fibers in the pulping process. The chips are passed through a refiner that has fixed and rotating disks operating under a stream of water. A wider range of species, including hardwoods, can be processed by the refiner pulping process. Sawdust and other saw mill wastes can also be used (figure 2-3).

Thermomechanical process (TMP) was developed as a modification of the refiner mechanical pulping process. In TMP, the wood chips are steamed for several minutes under pressure and subsequently refined in one or two stages. The lignin is softened by heating the wood chips with pressurized steam before they are refined (i.e., blended by passing the fiber through rapidly rotating disks). The refined wood pulp, although still weaker than chemical pulp, makes a stronger paper than groundwood or refiner pulp with only a small sacrifice in yield but with large energy requirements. Some newsprint is now produced wholly from thermomechanical pulp, thus eliminating the need for the addition of chemical pulp often needed for strengthening paper made from mechanical pulp.

The neutral sulfite semichemical (NSSC) pulping process is used at a number of U.S. mills to produce courser-grade products such as corrugated board, which has a yield of about 75 percent of the wood raw material. In NSSC pulping, wood chips are softened by briefly cooking them in a neutral sodium or ammonium sulfite solution and then separating the fibers (defibrating) in a refiner (see also *Sulfite Pulping* below).

Recycling can effectively reduce the consumption of both wood raw material and energy when used in conjunction with other mechanical pulping processes. It does so, however, with some sacrifice in paper strength. Recycled pulp is manufactured from wastepaper that is processed into paper stock. A small proportion of the paper stock (5 to 10 percent) is de-inked, usually with caustic soda-based chemicals. Most recycled paper, however, is pulped without de-inking. Pulping is accomplished through violent agitation and shearing action performed at high temperatures. The paper produced from recycled pulp is generally weaker than papers from virgin materials, because of the breakdown of the used fibers and loss of fiber bonding.

Figure 2-3—Refiner Groundwood Pulp Mill Process



SOURCE: Allan M. Springer, *Industrial Environmental Control: Pulp and Paper Industry* (New York, NY: John Wiley & Sons, 1986), p. 148.

Three major developments in mechanical pulping technologies show promise for improving pulp quality: 1) pressurized groundwood pulping, 2) chemical thermomechanical pulping, and 3) hardwood chemical mechanical pulping. All of these technologies have reached some stage of commercialization. Chemical thermomechanical pulping is currently used at several U.S. mills. Improvements in mechanical pulping show promise for improving the quality (strength characteristics) of paper now produced by mechanical processes. The resulting higher quality mechanical pulps may displace the kraft pulps that are currently mixed with mechanical pulps to improve paper strength.

Pressurized Groundwood Pulping—In pressurized groundwood pulping, debarked logs are fed to the grinding wheel through a heated, pressurized chamber. The heat and pressure help separate the fiber, thus breaking fewer fibers in the grinding process and improving pulp quality. Paper produced from pressurized groundwood pulp is more tear-resistant than paper made from stone-ground pulp, but is slightly inferior to that of thermomechanical pulp. Pressurized groundwood pulping may have the potential for displacing some high-quality chemical pulps in the manufacture of newsprint and other printing papers.

Chemical Thermomechanical Pulping— Chemical thermomechanical pulping involves treating softwood chips with mild sulfite solutions to modify the lignin and partially delignify the wood prior to grinding in a refiner. This "sulfonation" treatment results in paper with higher tear resistance than thermomechanical, refiner, or stone-ground pulps. Pulp yields decrease slightly to between 85 and 90 percent with chemical thermomechanical pulping, but these yields are still higher than chemical pulping (40 to 56 percent).

Hardwood Chemical Mechanical Pulping— Mechanical methods for producing pulp from hardwood species involve pretreating hardwood chips with hydrogen peroxide or sodium hydroxide and processing them like refiner mechanical pulps. Both hardwoods and softwoods have been successfully pulped by this method, with fiber recoveries in the 80 to 90 percent range. Pulp produced by hardwood chemical mechanical pulping can be used to produce newsprint and printing papers.

Chemical Pulping

Chemical pulping involves treating wood chips with chemicals to remove the lignin and hemicellulose, thus separating and cleaning the fibers. Delignification gives the fibers greater flexibility, resulting in a substantially stronger paper (because of greater contact between the fibers in the finished sheet) than can be manufactured from high-lignin fibers produced by mechanical pulping. Paper strength and durability is gained at the expense of fiber yield. Chemical processes may yield only half the fiber that can be recovered by the use of mechanical pulping techniques.

Two major chemical pulping processes are currently in commercial use: 1) kraft (sulfate) pulping, and 2) sulfite pulping. The kraft process dominates the pulp and paper industry, accounting for 76 percent of the pulp produced for paper and paperboard in 1984.[3] Paper produced from kraft pulp accounts for most of the bleached boxboard and linerboard used by the packaging industry (which consumes about 58 percent of the paper in the United States). Bleached softwood kraft pulps are often mixed with mechanical pulps to add strength to newsprint and printing papers. Bleached hardwood kraft pulps are added to bleached softwood pulp to improve printability for specialty paper products like magazine stock and coated papers. Both kraft pulp and sulfite pulp can be used for the production of dissolving pulp, which is used for the production of rayon and acetates.

Kraft Pulping—Kraft pulping involves treating wood chips and sawdust with a sodium sulfide and sodium hydroxide solution (see figure 2-1). The highly alkaline chemical and wood mixture is cooked with steam under pressure (digested) for between 1 and 3 hours. Digestion may be either a continuous process or treated in discontinuous "batches." Most of the lignin and some of the hemicellulose is dissolved, leaving the remaining cellulose fibers separated.

The cooking liquor containing the dissolved lignin and other extractives (black liquor) is routed to a chemical recovery plant where the lignin and

[3]*Lockwood's Directory of the Paper and Allied Trades 1986* (New York, NY: Vance Publishing Corp., 1986), p. 1.

organic wastes are burned to produce energy needed in the pulping process. Valuable extractives (e.g., turpentine, tall oil, and resin) are separated for sale as commodity chemicals. Process chemicals are recovered with only a relatively small loss in volume, and after replenishment with sodium salts, they are returned to the digester for reuse.

The brown pulp (brown stock) from the digester is washed, screened, and passed through a battery of cleaners. If the pulp is to be bleached, it is "thickened" by removing excess water and sent through a series of bleach operations. These can vary widely in the type of chemicals used and their sequence. Bleached pulp is then ready for the paper making process.

Both softwood and hardwoods can be pulped by the kraft process. Fiber recovery is largely a function of the wood species used, the time and temperature of cooking, the degree of bleaching, and the paper strength required. Generally, kraft pulp recoveries from softwoods are approximately 47 percent for unbleached pulp and 44 percent for bleached.[4] Hardwood recoveries range from 50 to 52 percent for unbleached kraft pulp to 50 percent for bleached.

Sulfite Pulping—Lignin can be dissolved by sulfonation with an aqueous solution of sulfur dioxide and calcium, sodium, magnesium, or ammonium bisulfite cooked at high temperature and pressure in a digester (see figure 2-4). There are four basic sulfite pulping processes currently in commercial use: 1) acid sulfite, 2) bisulfite, 3) neutral sulfite, and 4) alkaline sulfite. The major differences between the sulfite processes are the levels of acidity and alkalinity of the sulfite chemical solutions used to break down the wood and remove the lignin.

Sulfite pulping processes are suitable only for species with low extractive contents (i.e., those low in tannins, polyphenols, pigments, resins, fats, and the like) because of the interference of these substances with the sulfite pulping process. Although calcium is the cheapest sulfite base available, it forms insoluble compounds that cannot be reclaimed economically. Thus, calcium-based pulping is seldom used. Because magnesium- and sodium-based chemicals are recoverable, and ammonium-based chemicals are less expensive and can be burned without harmful environmental effects, they are the most frequently used.

Sodium-based sulfite pulping can consist of multistage cooking, successive stages of which differ in acidity. Because one stage optimizes chemical liquor penetration and the other the removal of lignin, more lignin may be removed with less fiber degradation, so that fiber yields are higher, fibers are stronger, and a wider range of wood species may be used. Sulfite pulping dissolves some of the hemicellulose as well as the lignin. Neutral sulfite pulping, using sodium and ammonium bases, recovers the largest proportion of fiber (75 to 90 percent) of all the sulfite pulping methods.

Sulfite pulp is a light color and can sometimes be used without bleaching if high brightness is not required. Unbleached sulfite pulp is often blended with groundwood and other high-yield mechanical pulps for strengthening newspaper stock. Sulfite pulp is easily bleached to very bright pulps for writing and printing paper. It is also used for the manufacture of dissolving pulps (through the further removal of hemicellulose) for the production of viscose rayon, acetate fibers and films, plastic fillers, and cellophanes.

Potential for New Pulping Technologies

The search for new pulping technologies and process improvements for established commercial technologies continues in the United States, Canada, Sweden, Finland, Japan, Germany, and elsewhere. In the United States, about $815 million is estimated to have been spent on pulp and paper research and development in 1987.[5] OTA could not determine what proportion of the R&D was directed at improving pulping technologies. Nearly all R&D is sponsored by the industry, with only $3 million (<0.4 percent) expended by the Federal Government.

Industry pulping R&D is largely focused on improving established pulping and bleaching processes rather than seeking new pulping technologies. Some of the research and development is driven by

[4]P.J. Hurley, *Comparison of Mills Energy Balance: Effects of Conventional Hydropyrolysis and Dry Pyrolysis Recovery Systems* (Appleton, WI: Institute of Paper Chemistry, 1978).

[5]Battelle Memorial Institute, *Probable Levels of R&D Expenditures in 1987: Forecast and Analysis* (Columbus, OH: Battelle, 1986), p. 11.

the need for broadening the raw material base in response to concerns over forest resources. Restrictions on water use and pollution control have contributed to the impetus for seeking process improvements.

Energy costs as reflected in both energy use by the industry and their impact on the cost of chemicals has led to process improvements in the past, although moderating energy prices have recently reduced these concerns. The emphasis on recycling to reduce the massive problems of solid waste disposal in metropolitan areas has also been an incentive to using more reclaimed material in paper manufacturing. Finally, the increasing cost of capital to rebuild aging sectors of the pulp and paper industry have fed the need for more R&D by the industry.

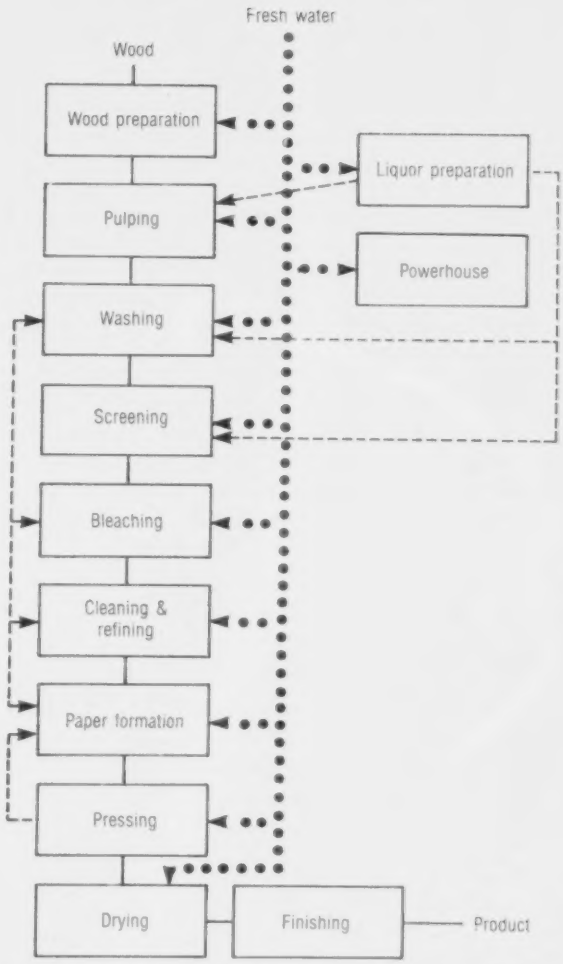
There are several reasons why major advancements in pulp and paper technology appear to be glacial in comparison to some other more rapidly advancing technologies. First, the pulp and paper industry is mature; the commercial technology, much of which was developed in the late 1700s and 1800s, has undergone evolutionary change, and satisfaction with the basic technology has led to little reason to fix something that does not appear to be broken. Concerns over future environmental problems and competition from other materials could change this, and to some degree already has.

Second, R&D is fragmented by the emphasis on process improvement, therefore few scientists and engineers focus on new pulping processes. In addition, many researchers specialize in one pulping process or another depending on the needs of a specific firm; few are able to consider all technological options or innovations for improving pulp yield or overall quality.

Third, R&D investment in incremental improvement in established processes is easier to sell to corporate directors than risky, long-term, radical changes. Large existing investments in plant equipment stretch the amortization period of old equipment and slow the acceptance of new processes that require substantial changes and alterations.

Finally, the absence of major government investment in long-range, high-risk R&D to seek new, innovative pulping and bleaching technologies may limit the advancements that could be made through collective R&D efforts. Individual firms have little incentive to undertake a major, long-term, high-investment R&D program to develop radically new technologies with uncertain payoff in the end, particularly in the current investment climate.

Figure 2-4—Sulfite Pulp Mill Process



SOURCE: Allan M. Springer, *Industrial Environmental Control: Pulp and Paper Industry* (New York, NY: John Wiley & Sons, 1986), p. 153.

Organosolv Pulping (Ester Pulping)—Organosolv pulping—sometimes called ester pulping—is a two-stage process involving hydrolysis (decomposi-

tion of the wood by dilute acids or enzymes) and the removal of lignin with an organic solvent, usually a mixture of alcohol and water. The still experimental process is suitable for both hardwoods and softwoods. Sawdust as a byproduct from lumber manufacture can also be pulped.[6] Pulp recovery from organosolv pulping ranges between 50 and 60 percent for hardwoods, and 40 and 45 percent for softwoods. Typical hardwood fiber recoveries compare favorably with those from kraft pulping.

Fibers produced by the organosolv process are weaker than those recovered by the kraft process. Thus, the papers produced from organosolv pulp are suitable for uses where strength is not the most important property (e.g., printing papers, fluff pulps, and dissolving pulp). Little waste is produced by the process, and low alcohols are recovered easily by distillation, thus requiring relatively low capital investment.[7] Commercial viability of this technology will require that markets be developed for byproducts of the process.

A commercial demonstration plant using the Alcell process developed by Repap Enterprises Corp. of Canada is currently under construction at Newcastle, New Brunswick. The 33-ton-per-day pilot plant will cost $65 million. The Canadian government is underwriting half the cost of the plant. Alcell is an alcohol cellulose organosolv process.

Hydrotropic Pulping—Hydrotropic solutions are aqueous salt solutions that impart greater solubility to slightly soluble substances (e.g., lignin) than does water at the same temperature. Sodium xylenesulfonate, a hydrotropic salt, has been used experimentally to delignify wood.[8] A hydrotropic pulping process was patented by Ralph H. McKee in 1943.[9] Laboratory pulping texts suggested that dissolution of lignin with aqueous sodium xylenesulfonate solutions of 30 to 40 percent had little or no effect on the strength of the pulp and yielded a high alpha cellulose content (important for dissolving pulp).

Pulping of poplar was conducted at temperatures of about 150 °C for 11 to 12 hours. Tests yielded 52 percent cellulose, compared to 47 percent from comparable sulfite pulp. Unlike sulfite or kraft pulping which uses contaminating inorganic chemicals, the lignin recovered through precipitation by hydrotropic pulping is relatively pure and is suitable for conversion to other chemical products. The process is not suited for resinous coniferous species, however, and comparatively little serious attention has been given to this process by the industry.

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[6]Theodor N. Keinert, "Oranosolv Pulping With Aqueous Alcohol," *TAPPI J.*, August 1974, vol. 57, p. 99 et seq.

[7]N. Sawyer, *Status of New Pulping Processes: Problems and Perspectives* (Madison, WI: U.S. Forest Products Laboratory, 1982), p. 10; see also Raymond W. Young and Kenneth W. Baierl, "Ester Pulping of Wood: A Revolutionary Process," *Southern Pulp & Paper*, November 1985, pp. 15-17.

[8]Ralph H. McKee, "Use of Hydrotropic Solutions in Industry," *Industrial and Engineering Chemistry*, vol. 38, No. 4, 1946, p. 382; see also Ralph H. McKee, "Comparison of Wood Pulping Process," *Pulp and Paper Magazine of Canada*, vol. 55, No. 2, 1954, pp. 64-66.

[9]U.S. Patent No. 2308564, Jan. 19, 1943.

Chapter 3

Environmental Considerations

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Chapter 3
Environmental Considerations

Pulp manufacture, like most chemical processes, results in emissions, effluents, and solid residues that must be disposed of. This study focuses on chlorinated bleached pulp mill waste effluents and residual chlorinated compounds in paper products (with emphasis on TCDD and TCDF), therefore air emissions and solid wastes[1] will not be considered here. Technologies for reducing the production of chlorinated organics in the pulping process are discussed in chapter 5.

CHLORINATED DERIVATIVES IN THE ENVIRONMENT—AN OVERVIEW

Effluents from bleached pulp mills contain a variety of substances, some of which exhibit a variety of effects in biological tests, such as genotoxicity, mutagenicity, or teratogenicity. These include resin acids and fatty acids, chlorinated phenols, and other chlorinated organic substances. The composition of bleaching effluent is extremely complex and varies from mill to mill depending on the wood species being pulped, the pulping technology, bleaching reagents, and waste treatment systems used.[2] Comparatively little is known about the actual composition of mill waste effluents, although substantial scientific effort has been spent on research. A screening and verification survey of pulp and paper mill effluents conducted by the Environmental Protection Agency (EPA) tentatively identified a number of chlorinated organic chemicals (table 3-1). The chlorinated components of the waste stream consist mostly of simple phenols, phenolic and carbohydrate oligomers (high and low molecular weight polymers), and neutral and acidic materials resulting from the breakdown of the phenolic rings in lignin.[3]

It has been estimated that no more than 10 percent of the total solids in the waste stream of a pulp bleaching plant contain chlorinated derivatives. However, their toxicity to aquatic biota has raised concerns among biologists.[4] Chlorinated mill wastes have only recently been focused on in the United States, although the toxicity of untreated, undiluted waste to aquatic biota is well documented in the scientific literature. A technical committee of Environment Ontario, the provincial environmental agency for Ontario, Canada, recently reviewed the available information on chlorinated organics and dioxin from mill waste. Based on its analysis, the committee recommended that Ontario adopt a long-term strategy aimed at completely eliminating the formation of organochlorines in kraft pulp mills.[5] The committee also concluded, however, that "chlorinated dioxins do not represent an immediate danger to human health and welfare," but it did note that heavy fish-eaters consuming fish caught downstream of some bleached kraft mills might exceed the acceptable daily intake of TCDD.

Sweden and Finland, with pulp and paper mills located adjacent to the Gulf of Bothnia and the Baltic Sea, have experienced environmental damage to marine life from chlorinated organic substances

[1]Solid waste disposal, particularly the disposal of contaminated sludge from biological treatment plants, is an important factor in the ultimate solution of safely disposing of dioxin. U.S. EPA information on pulp mill sludge disposal provided to OTA by Karen Florini, Environmental Defense Fund, shows that of the 104 bleached chemical pulp mills in the United States, 54 dispose of sludge in landfills, 20 use surface impoundments, 20 incinerate the sludge, 6 convert it to compost or other salable products, 6 apply it to the land as a soil amendment, and 2 dispose of it by other means (total exceeds 104 because some mills use more than one method of disposal). The subject of solid waste disposal has many aspects that range far beyond the focus of this study, including disposal of contaminated municipal sewage sludge, disposal of toxic and hazardous materials, and disposal of incinerator residues. OTA has published several reports on related topics: *Wastes in Marine Environments*, OTA-O-335, April 1987; *From Pollution to Prevention: A Progress Report on Waste Reduction*, OTA-ITE-347, June 1987; *Technologies and Management Strategies for Hazardous Waste Control*, OTA-M-197, March 1983; *Serious Reduction of Hazardous Waste* OTA-ITE-318, September 1986.

[2]Between 250 and 300 chemicals have been identified in pulp mill effluents. Many of these are chlorinated compounds. Leena R. Suntio, Wan Ying Shui, and Donald Mackay, "A Review of the Nature and Properties of Chemicals Present in Pulp Mill Effluents," *Chemosphere*, vol. 17, No. 7, 1988, pp. 1249-1290.

[3]Carlton W. Dence and Goran E. Annergren, "Chlorination," *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI, 1979), p. 69.

[4]Ibid., p. 71.

[5]Environment Ontario, *Stopping Water Pollution at its Source: Kraft Mill Effluents in Ontario*, Report of the Technical Advisory Committee, Pulp and Paper Sector, Municipal/Industrial Strategy for Abatement (Toronto, Ontario: Environment Ontario, 1988), pp. 1-2.

Table 3-1—Major Chlorinated Derivatives Identified in Pulp and Paper Mill Effluents

chlorobenzene
1,1,1-trichloroethane
trichlorophenol *
2,4-dichlorophenol
dichlorobromomethane
chlorodibromomethane
trichloroethylene
monochlorodehydroabietic acid
2,3,7,8-tetrachlorodibenzo-p-dioxin *
1,2-dichloroethane *
1,1,2,2-tetrachloroethane **
chloroform **
methylene chloride **
trichlorofluoromethane
tetrachloroethylene *
3,4,5-trichloroguaiacol
9,10-dichlorostearic acid
2,3,7,8-dibenzofurans*

* Listed as carcinogens in the *Fourth Annual Report on Carcinogens*, U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program, 1985.

** Listed as carcinogens by the National Institute of Occupational Safety and Health; see Office of Technology Assessment, *Identifying and Regulating Carcinogens—Background Paper* (Chelsea, MI: Lewis Publishers, 1987), p. 84.

SOURCE: U.S. Environmental Protection Agency, *Development Document for Effluent Limitations Guidelines and Standards for the Pulp, Paper, and Paperboard and the Builders' Paper and Board Mills—Point Source Categories*, EPA 440/1-82/025 (Washington, DC: 1982), p. 46.

released into coastal waters.[6] Sweden's National Environmental Protection Board (Naturvardsverket) estimates that Scandinavian pulp and paper mills contribute between 300,000 and 400,000 tons of chlorinated organic materials to the coastal waters of Sweden, Finland, and Norway annually.[7] Evidence of environmental harm in the estuaries of the Baltic Sea (including the accumulation of dioxin in the flesh of food fish), where water circulation and exchange are extremely slow, has led the Swedish Government to consider regulations to reduce the amount of chlorinated organic substances produced by bleached sulfate pulp mills by imposing regulations that require the use of oxygen bleaching and increased use of chlorine dioxide bleach in place of chlorine gas. Sweden is also considering steps to promote the use of closed-cycle processes that would significantly reduce or even eliminate the release of chlorinated wastes to the environment.

The Swedish experience, where biological waste treatment is less prevalent, contrasts with that of the United States where nearly all bleached kraft pulp mills use secondary biological treatment to reduce the biological and chemical oxygen demands of wastewater. In the course of biological treatment, many potentially toxic substances are removed and concentrated in the treatment sludge.[8] Many Swedish mills, on the other hand, do not use biological waste treatment, and discharge their effluent directly into the environment or use only primary waste treatment.

The overall release of chlorinated organic compounds from pulp and paper mills has received less attention in the United States up to now. Instead, the major concern arose over TCDD and TCDF that are produced along with other chlorination products during bleaching cycles and are considered to be potentially harmful to human health.[9] A similar pattern of concern over dioxin developed in Canada. A recent report on pollution from kraft mill effluents published by Environment Ontario warned against focusing too closely on dioxins as a result of media publicity, because it "may divert energies from productive avenues of pollution control into blind alleys of ill-conceived, routine, and expensive surveys of 'dioxin' concentrations."[10]

Products containing TCDD were at one time used extensively as herbicides (agent orange, 2,4,5-T). They are also produced as byproducts from the incineration of municipal and industrial waste, the combustion of wood in home furnaces, stoves, and fireplaces, metal smelters, and the incomplete combustion of dielectric fluids (PCBs) in electrical transformers. The use of dioxin-containing materials in industrial processes has since been significantly

[6]Committee for the Gulf of Bothnia, *Water Pollution Problems of Pulp and Paper Industries in Finland and Sweden*, Report of the Special Working Group, Naturvardsverket Rapport 3348, in English (Solna, Sweden: Baltic Marine Environment Protection Commission, 1987), app. 3.

[7]National Swedish Environmental Protection Board, *Action Plan for Marine Pollution* (Solna, Sweden: Naturvardsverket, 1987), p. 27.

[8]A well-maintained, properly operated biological waste treatment plant can remove 30 to 50 percent of chlorination products and about 85 percent of TCDD and TCDF that is retained on suspended solids. Preliminary, unpublished research by the industry reported at the OTA November 1988 workshop indicates that it may be possible to remove up to 90 percent of the chlorinated organics with supplemental chemical treatment. This work is still experimenal.

[9]"Dioxins" and "furans" refer generically to chlorinated dibenzo-para-dioxins (CDD) and chlorinated dibenzofurans (CDF), respectively, that have one to eight chlorine substituents.

[10]Environment Ontario, op. cit., note 5, pp. 1-19.

curtailed, but their inadvertent production through chemical and industrial processes, and as combustion products continues.

DIOXIN[11]

Dioxin, as generally referred to, is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). It is the most toxic of 75 chlorinated dioxins and over 135 chlorinated furans (TCDFs).[12] Dioxin is a byproduct of, or a contaminant in, manufactured materials. The chemical reactions and conditions under which they are formed in the pulp mill are not completely understood. TCDD was never produced as such intentionally except in small experimental quantities for research. In the United States, TCDD largely earned its reputation as a "bad actor" in the Agent Orange controversies following the use of herbicides as defoliants during the Vietnam War.

Agent Orange was a mixture of the herbicides 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,4-dichlorophenoxyacetic acid (2,4-D). These same chemicals were extensively used in forestry and agriculture with little recognition of the health risks that may be related to the dioxin that 2,4,5-T contained as an incidental ingredient (2,4,5-T is no longer manufactured in the United States). The exposure of military personnel to these chemicals in Vietnam raised the consciousness of the public about the health risks of dioxins when returning veterans blamed a number of their health problems and those of their families on past exposure to Agent Orange while serving in the military.

How serious a human health threat is the exposure to dioxins? On purely scientific bases, the question of human risk has not yet been definitively answered. Epidemiological data are incomplete and difficult to interpret. No study thus far has conclusively linked dioxins to the death of a human, or to a human disease other than chloracne, or conclusively related exposure to dioxin to cancer (although the carcinogenic potential is considered to be "probable"), or to miscarriages.[13] Abnormal behavior, genetic effects, immunological problems, enzymatic disfunctions, and reproductive problems associated with dioxin exposure have been considered, but studies have not confirmed dioxins to be the cause.

With regard to certain—but not all—laboratory test animals, dioxin has been shown to be extremely toxic and lethal at low levels. Procedures for extrapolating from animal effects to humans are controversial. There is, however, sufficient scientific evidence to suggest that human exposure to dioxin should be minimized within acceptable levels of risk pending a better understanding of its health implications. The public perceives dioxins to be dangerous and a major health risk as a result of publicity surrounding the Agent Orange controversy, the Times Beach incident, the Love Canal, and problems related to the disposal of hazardous wastes. The regulatory agencies have opted for a conservative approach to regulating dioxins.

Research on rainbow trout, a species often used to gauge the toxicity of chemicals, suggests that TCDD and TCDF can cause mortality, reduced growth, and abnormal behavior during the fishes' early life stages. TCDD was judged to be 10,000 times more toxic than the pesticides endrin or toxaphene, while TCDF was 1,000 times more toxic.[14] Bioconcentration factors (BCF) for TCDD were found to be much higher than originally estimated. TCDD accumulated to about 39,000 times the ambient concentration of the water, and TCDF between 2,640 and 4,449 times (but dioxin seems to concentrate in the gut and inedible parts of fish). It has also been shown that similar preferential bioaccumulation or magnification of TCDD and TCDF occurs in aquatic birds.[15] However, the effects of TCDD and TCDF on

[11]This discussion of the human health effects of dioxin is not intended to be definitive or analytical with regard to the dangers of dioxin. Rather, it is an encapsulation of other recent surveys of existing knowledge about dioxin and its congeners.

[12]Tests on laboratory animals suggest that if the toxicity of 2,3,7,8-TCDD is assigned the value of 1.0, the toxicity of 2,3,7,8-TCDF is 0.1. Other dioxins and furans also generally have toxicities that are estimated to range from one-tenth to one-thousandth that of 2,3,7,8-TCDD.

[13]U.S. Environmental Protection Agency, *National Dioxin Study*, EPA/530-SW-87-025 (Washington, DC: 1987), pp. 1-8.

[14]Paul M. Mehrle et al., "Toxicity and Bioconcentration of 2,3,7,8- Tetrachlorodibenzodioxin and 2,3,7,8 Tetrachlorodibenzofuran in Rainbow Trout," *Environmental Toxicology and Chemistry*, vol. 6, 1988, pp. 47-62.

[15]D.L. Stalling et al., "Patterns of PCDD, PCDF, and PCB Contamination in Great Lake Fish and Birds and Their Characterization by Principal Component Analysis," *Chemosphere*, vol. 14, No. 6/7, 1985, pp. 627-643.

reproduction, survival, and behavior of bird populations is uncertain.[16]

DIOXIN AND PULP AND PAPER MANUFACTURE

National Dioxin Study

The National Dioxin Study (NDS), a 2-year effort to explore the extent of dioxin contamination in the environment, detected the presence of TCDD and TCDF in fish and bottom sediment samples collected downstream of several U.S. pulp mills.[17] Fish samples for the NDS were selected in three ways:

- 90 sites were selected statistically,
- 305 sites near urban and industrial areas were nominated by EPA's Regional Offices or the Office of Water Regulations and Standards (OWRS), and
- 57 estuarine or coastal sites were sampled.

Of the 90 sites sampled statistically for fish contamination, 17 showed detectable levels of TCDD up to 19 parts per trillion (ppt) in composite whole fish samples (see box 3-A).[18] Nearly one-third of the 305 regional samples showed detectable levels of dioxin in whole fish samples. These sample sites included rivers, lakes, and some coastal and estuarine waters. TCDD levels in some samples ranged up to 85 ppt. Only 4 of the 57 estuarine and coastal sites sampled had detectable levels of dioxin in fin fish or shellfish, and these ranged between 1.08 and 3.5 ppt.

About 80 percent of the whole fish sampled from sites in the Great Lakes were found to have detectable levels of dioxin. A multitude of potential dioxin sources are within the watershed of the Great Lakes and the turnover and flushing of the waters within the Lakes are extremely slow. Outside the Great Lakes, detectable dioxin levels were most frequently found in the major river systems that flow through industrial and urban areas. Advisories have been issued by Wisconsin, Maine, and Louisiana warning of possible risk of eating contaminated fish.

Box 3-A—Detection Limits and Levels of Dioxin Contamination

Determining the amount of dioxin in the natural environment requires sophisticated analytical procedures and careful statistical sampling and sample preparation. High resolution gas chromatography and mass spectrometry are used to quantify dioxin levels. Gas chromatography separates the dioxins from other compounds by selectively adsorbing the dioxins (based on their specific molecular weights) on an adsorbent such as activated charcoal, alumina, or silica gel. Mass spectrometry separates the dioxins specifically and quantitatively according to their atomic weights. These technologies can measure dioxins in the range of parts per quadrillion (ppq) in water samples, but this level of detection is still considered experimental for most biological samples.

EPA selected a nominal detection limit of one part per trillion (ppt) for fish and soil samples collected in the course of the National Dioxin Study. This sensitivity pushed the limits of the state-of-the-art in analytical technology. Comprehending parts per quadrillion and parts per trillion can boggle the mind. One ppt is equivalent to 1 second in 32,000 years. One ppq is equivalent to 1 second in 32,000,000 years. The potency of dioxin makes measurements at this minute level of resolution important.

The Food and Drug Administration (FDA) recommends that consumption of fish be limited if dioxin content exceeds 25 ppt, and consumption is banned when levels reach 51 ppt. In general, EPA found that dioxin levels of fish fillets—the edible portions of the fish—had dioxin levels below the detection limits even though whole fish samples may be judged to be contaminated.

At two-thirds of the sites where dioxin was detected, the maximum values encountered were below 5 ppt. At only four sites did dioxin levels exceed 25 ppt (the level at which FDA recommends that fish consumption be limited). The high-level sites were located in the Androscoggin River at Lewiston, Maine (29 ppt), and the Rainy River at

[16]J.E. Elliot et al., "Levels of Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans in Eggs of Great Blue Herons (*Ardea herodias*) in British Columbia, 1983-1987: Possible Impacts on Reproductive Success," Progress Notes No. 176, Canadian Wildlife Service, April 1988, p. 7.

[17]U.S. Environmental Protection Agency, *National Dioxin Study*, EPA/530-SW-87-025 (Washington, DC: 1987), pp. III-32-33.

[18]Ibid., pp. III-29.

International Falls, Minnesota (85 ppt), both of which are located downstream of pulp and paper mills.[19] Additional investigations at these sites showed dioxin levels of up to 414 ppt in waste treatment sludges from the mills.

As a follow-on to the NDS, EPA is investigating other chemical pollutants that might accumulate in fish. The National Bioaccumulation Study (NBS), which is currently underway, is focusing on a subset of "priority" pollutants selected from among 400 potential chemicals. These include non-conventional pesticides, semi-volatile organic chemicals known to accumulate in human fatty tissue, agricultural chemicals, industrial chemicals, and those in pulp mill effluents. Four hundred sites are being sampled in targeted industrial, urban, and agricultural areas and below pulp mills. Approximately 95 percent of the fish samples have been collected. Of the 75 samples that have been analyzed from fish collected below pulp mills, 67 are reported to have dioxin above detectable levels. Samples from 10 mill sites report TCDD and TCDF concentrations in fish fillet tissue above the acceptable FDA limits of 25 ppt.[20]

Recent data from the NBS based on fish sampled from 18 southern rivers receiving mill wastes showed accumulations of dioxin in whole fish ranging from about 1 ppt up to 164 ppt. Most whole fish samples had dioxin levels between 10 and 40 ppt. Three whole fish samples had levels exceeding 100 ppt. The edible part of the fish (fillets) contained much lower dioxin levels and none exceeded FDA's 25 ppt acceptable limits, although one fish showed a level of 24 ppt of dioxin.[21]

EPA/Paper Industry Joint Five-Mill Study

The results of the National Dioxin Study indicated that effluent from the manufacture of pulp can introduce detectable levels of dioxin into the environment. This prompted the U.S. pulp and paper industry, through the National Council of the Paper Industry for Air and Stream Improvement, and EPA to undertake a joint investigation of five bleached kraft pulp and paper mills in 1986.[22] The cooperative screening study focused on three mills known to have dioxin in their waste sludge (all of the mills sampled used the activated sludge waste treatment process) plus two additional mills that were volunteered by their firms to provide broader geographical coverage (table 3-2). The results of the cooperative five-mill study indicated that the bleaching of kraft pulp with chlorine and chlorine derivatives is responsible for the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF as byproducts of the pulping process.

Dioxin in Bleached Pulps

Sensitive gas chromatographic procedures were used to distinguish between the amounts of 2,3,7,8-TCDD and the related isomers of chlorinated furan (2,3,7,8-TCDF) in the bleached pulp and mill wastes. TCDD was detected in seven of nine bleached pulps sampled, at levels up to 51 ppt. The median TCDD content was 4.9 ppt, and the mean was 13 ppt.[23] TCDF was found in eight of nine pulp samples at levels ranging from below detection limits to 330 ppt. The median TCDF content was 50 ppt, and the mean was 93 ppt.

Dioxin in Bleach Plant Wastewaters

Wastewater from each stage of the pulp bleach sequence was systematically sampled at each mill. TCDD was detected in wastewaters at three of the five mills, and TCDF was detected at four of the five mills sampled. The greatest discharge of both TCDD and TCDF was associated with the caustic extraction stage, which serves to flush away the lignin and other coloring agents that are mobilized during the bleaching stages. Lesser amounts of TCDD and TCDF were detected in the wastewaters of the hypochlorite bleaching stage and the chlorination bleaching stages (see table 3-3).

[19]Ibid., pp. III-30.

[20]Steven Croner, U.S. Environmental Protection Agency, unpublished materials presented at OTA dioxin workshop, Washington, DC, Nov. 14-15, 1988.

[21]National Bioaccumulation Study data provided to OTA by Karen Florini, Environmental Defense Fund, Washington, DC, Feb. 6, 1989.

[22]G. Amendola et al., "The Occurrence and Fate of PCDDs and PCDFs in Five Bleached Kraft Pulp and Paper Mills," Presented at the Seventh International Symposium on Chlorinated Dioxins and Related Compounds, Las Vegas, NV, October 1987.

[23]Ibid., p. 8.

Table 3-2—Characteristics of the Bleached Kraft Pulp and Paper Mills Used in the Five-Mill EPA/Industry Cooperative Dioxin Screening Study

Mill	Furnish (in percent)		Daily capacity	Bleach sequences		Daily effluent production (million
	Hardwood	Softwood	(tons)	Hardwood	Softwood	gallons)
I	85	15	500	CE_OH & CE_OHHP	CE_OHHP	23
II	20	80	775[a]	CEHED	CEHED	36
III	100	NA	1,000	C/DE_OD	—	36
IV	NA	100	400[b]	—	CEH	18
V	30	70	1,200[c]	C_DE_OH/D	C_DE_OH/D	41

NA = Not applicable

[a] Can also produce 300 tons per day of refiner mechanical groundwood pulp.
[b] Has additional capacity to produce 830 tons per day of groundwood.
[c] Also can produce 130 tons of groundwood daily.

SOURCE: G. Amendola et al., "The Occurrence and Fate of PCDDs and PCDFs in Five Bleached Kraft Pulp and Paper Mills," paper presented at the Seventh International Symposium on Chlorinated Dioxins and Related Compounds, Las Vegas, NV, October 1987.

Table 3-3—Concentration of TCDD and TCDF in Bleach Plant Wastewater

Bleaching stage	TCDD (ppt)			TCDF (ppt)		
	Range	Median	Mean	Range	Median	Mean
Chlorination	0.01-0.24	0.04	0.07	0.06-3.8	0.24	0.65
Caustic wash	0.01-3.6	0.24	1.00	0.06-33.0	0.78	7.4
Hypochlorite	0.02-1.9	0.20	0.40	0.09-9.2	0.59	2.3
Chlorine dioxide	0.01-0.03	ND	ND	0.01-0.13	ND	ND

ND = Not detectable

SOURCE: G. Amendola et al., "The Occurrence and Fate of PCDDs and PCDFs in Five Bleached Kraft Pulp and Paper Mills," paper presented at the Seventh International Symposium on Chlorinated Dioxins and Related Compounds, Las Vegas, NV, October 1987.

Dioxin in Wastewaters and Sludges

Comparisons among the mills indicated that the TCDD and TCDF contents of pulp and wastewater differed greatly from mill to mill. TCDD produced in the pulp bleaching process can be transported to the environment as a residual in finished pulp, in the sludge recovered in the wastewater treatment process, or as treated effluent released into streams and pond (table 3-4). TCDD was found in wastewater treatment sludges at each of the five mills sampled.[24] Analyses of wastewater from the paper machines showed that some of the dioxin produced in the bleaching process was passed through to the paper making process.

Continuing Efforts

Although the five-mill cooperative survey confirmed that chlorinated bleaches can produce dioxins in the manufacture of bleached wood pulp, the study revealed great variability in dioxin concentrations among the mills and within the pulps, waste sludge, and treated effluents. The results demonstrated the need for a comprehensive and systematic survey of the receiving waters and biota below the waste outlets of U.S. pulp mills in order to better understand the scope and intensity of the environmental loading of TCDD. The survey also indicated that more detailed information was needed about dioxin levels at various steps in the pulping process and in the bleaching sequence.

EPA has recently negotiated a cooperative agreement with the American Paper Institute (API) and the National Council of the Pulp and Paper Industry for Air and Stream Improvement (NCASI), both associated with the U.S. pulp and paper industry, to survey all 104 domestic pulp mills that manufacture chemical bleached pulp for production of dioxin and

[24] U.S. Environmental Protection Agency, *U.S. EPA/Paper Industry Cooperative Dioxin Screening Study*, EPA-440/1-88-025 (Washington, DC: 1988), p. viii.

Table 3-4—Mode of Environmental Release of TCDD and TCDF From Pulp and Paper Mills (percent)

Source	Mill I	II	III	IV	V
2,3,7,8-TCDD					
Bleached pulp	19	66	—	30	57
Waste sludge	16	16	100	70	22
Treated effluent	65	18	—	—	21
2,3,7,8-TCDF					
Bleached pulp	19	56	60	31	55
Waste sludge	17	20	36	69	22
Treated effluent	64	24	4	—	23

SOURCE: G. Amendola et al., "The Occurrence and Fate of PCDDs and PCDFs in Five Bleached Kraft Pulp and Paper Mills," paper presented at the Seventh International Symposium on Chlorinated Dioxins and Related Compounds, Las Vegas, NV, October 1987.

furan isomers.[25] In addition, an industry study will undertake a detailed analysis of dioxin levels and bleaching processes at selected pulp mills.

The study will consider the full range of factors that might affect the production and dispersal of dioxins, including annual effluent flow, wastewater treatment, sludge disposal practices, bleach plant operations, and an analysis of dioxin contents of effluents, pulps, and sludges. Detailed analyses of dioxin levels in 25 bleach lines will be included. The study began in the summer of 1988, and is expected to be completed in the summer of 1989.

In a related effort, an EPA-led interagency group has undertaken a Multi-Media Risk Study that will utilize data collected in the EPA/Industry 104-mill study. Under a court-approved consent agreement to consider dioxin in paper, EPA is attempting to estimate the cumulative risk of dioxin from this source in all media—pulp, sludge, and effluent.[26] Data collected in the 104-mill study, and estimates of migration rates of TCDD and TCDF from paper products adjusted by product-use scenarios, will be used to determine whether or not there is a human risk from dioxin in pulp and paper.[27] The consent decree also requires EPA to undertake an assessment of environmental risks as well as human risks. The Food and Drug Administration (FDA) and Consumer Safety Product Commission (CSPC) have initiated product risk assessments that will become part of the interagency multi-media study.

DIOXIN IN PULP AND PAPER PRODUCTS

The finding of TCDD and TCDF in bleached pulp samples raised questions as to whether residual TCDD might also find its way into finished paper products and present a potential health risk to consumers through dermal contact (it did not consider other routes of exposure). The NCASI commissioned Envirologic Data, Inc. to assess the potential risks[28] to human health from skin exposure to a variety of bleached pulp products, including disposable diapers, facial tissue, toilet tissue, sanitary napkins, and paper towels.[29]

The results of Envirologic Data's risk assessment of concentrations of TCDD found in paper products were related to a lifetime cancer risk of one in a million in the general population—a regulatory standard commonly used by the EPA and the FDA to gauge risk. Based on this measure of risk, a "virtually safe concentration" of TCDD equivalents was calculated for the various products tested (table 3-5).

[25]See *Federal Register*, vol. 53, No. 27, Feb. 10, 1988, p. 3937; EPA Office of Water Regulations and Standards, and Office of Toxic Substances, U.S. EPA/Paper Industry Cooperative Dioxin Study—Tier 1, Fact Sheet, Feb. 4, 1988.

[26]See, *Environmental Defense Fund & National Wildlife Federation* v. *Thomas*, No. 85-0973 (D.D.C., consent decree entered July 27, 1988).

[27]Dwain Winter, U.S. Environmental Protection Agency, communication at the OTA dioxin workshop, Washington, DC, Nov. 14-15, 1988.

[28]Risk assessment is the characterization of the probability of potentially adverse health effects from human exposure to environmental hazards. The risk assessment process consists of four steps: 1) hazard identification, 2) dose-response assessment, 3) exposure assessment, and 4) risk characterization. NCASI used EPA's guidelines for Carcinogen Risk Assessment as a framework for the dioxin dermal exposure study.

[29]National Council of the Paper Industry for Air and Stream Improvement, *Assessment of Potential Health Risks From Dermal Exposure to Dioxin in Paper Products*, Technical Bulletin No. 534 (New York, NY: 1987), p. 107.

Table 3-5—Safe-level Concentrations of TCDD in Paper Products

	Calculated TCDD equivalent (in ppt)		
	Female	Male	Measured
Bleached pulps			5[a]
Communication paper			13[b]
Clerical worker	9,000	9,100	
Manager	4,200	4,300	
Personal care products[c]			
Disposable diapers			0[c]
Conventional	540,000	540,000	
Superabsorbent	2,000,000	2,000,000	
Facial tissue			
Normal use	66,000,000	79,000,000	
Makeup	230,000		
Toilet tissue	27,000,000	65,000,000	
Sanitary pads	63,000,000		
Paper towels	7,900,000	9,500,000	
Composite personal care products[d]	160,000	510,000	
Combined communication papers and personal care products			4
Clerical worker	8,500	8,900	
Manager	4,100	4,200	

[a] Measured in 7 pulps with levels of dioxin from less than 1 ppt to 51 ppt, with a median of 4.9 ppt.

[b] Measured in bond paper.

[c] No TCDD detected in disposable diapers at detection limits of 2.1 and 2.6 ppt.

[d] Excluding superabsorbent disposable diapers.

SOURCE: National Council of the Paper Industry for Air and Stream Improvement, *Assessment of Potential Health Risks From Dermal Exposure to Dioxin in Paper Products*, Technical Bulletin No. 534 (New York, NY: 1987), p. 107.

Calculated safe levels for bond paper, newspaper, and other paper used for communications ranged from 4,200 ppt of TCDD for female managers to 9,100 ppt for male clerks. Safe levels for personal care products were calculated to range from 230,000 ppt of TCDD for female facial tissue used for makeup removal to 79,000,000 ppt for facial tissue by males. Safe levels for paper towels were calculated at 7,900,000 ppt for females and 9,500,000 ppt for males. Toilet tissue safe limits for females were calculated at 27,000,000 ppt for females and 65,000,000 ppt for males. Actual concentrations of TCDD in samples of bond paper were detemined to be about 13 ppt; in paper towels, 4 ppt; and no detectable TCDD was measured in disposable diapers.

NCASI published the results of an assessment of potential exposure to dioxin from coffee brewed using bleached coffee filters in May 1988.[30] Based on an assumed consumption profile for an average and heavy coffee drinker and assuming that 65 to 90 percent of the dioxin migrated from the filter, NCASI concluded that the calculated dioxin TEQs for a risk ranging from zero to one in one-million to be between 20 ppt TCDD TEQs for average coffee drinkers to 11 ppt TCDD TEQs for heavy coffee drinkers. The coffee filters tested had TEQ dioxin contents ranging from 2.2 to 6.6 ppt.

An assessment of dioxin in food packaging paper products has been initiated.[31] NCASI commissioned ENVIRON, Inc. to undertake the evaluation. A number of food contact products are scheduled to be undergo risk assessment, such as paper cups and plates, convenience food packaging, paper towels, and pizza boxes. NCASI has put the project on hold pending the development of acceptable test procedures to determine the absorption of dioxin into fatty foods. The assessment will resume when test protocols are developed

Scientists at Health & Welfare Canada, a government agency, reported in August 1988 that they had

[30]National Council of the Paper Industry for Air and Stream Improvement, *Assessment of the Risks Associated With Potential Exposure to Dioxin Through the Consumption of Coffee Brewed Using Bleached Paper Coffee Filters*, Technical Bulletin 546 (New York, NY: 1988), p. 34.

[31]National Council of the Paper Industry for Air and Stream Improvement, *First Progress Report on the Assessment of Potential Health Risks From Use of Bleached Board and Paper Food Packaging and Food Contact Products*, Special Report 87-11 (New York, NY: 1987), p. 27.

detected 0.04 ppt of TCDD and 0.75 ppt of TCDF in whole milk packaged in plasticized bleached paper cartons.[32] They reported no similar levels in milk packaged in non-bleached paper containers. NCASI is currently collaborating with Canadian scientists to confirm these findings.

[32]John J. Ryan, Food Research Division, Health Protection Branch, Health & Welfare Canada, Ottowa, Canada, paper presented at the International Dioxin Symposium, Umea, Sweden, August 1988.

Chapter 4

Pulp Bleaching Technology

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Chapter 4

Pulp Bleaching Technology

THE BLEACHING PROCESS

Bleaching is the treatment of cellulosic fiber with chemicals to increase brightness (see box 4-A). Brightness may be achieved by either lignin removal (delignification) or lignin decolorization. Lignin remains a major constituent of pulp even after digestion by chemical pulping. For example, kraft pulp may contain up to 6 percent lignin based on its dry weight.[1] Unbleached groundwood spruce pulp may contain 27 percent lignin.

If chemical pulping removes the lignin from wood fibers, why then does some lignin remain after the pulping process? The strength of paper is largely due to the chemical bonds (hydrogen bonds) formed between cellulose fibers. Although longer and more severe pulping might remove more of the lignin, thus reducing the amount of bleaching needed, the cellulose molecules might be degraded and their bonding power diminished. Should this happen, the strength of the pulp would be reduced. The removal of lignin by bleaching is regarded as a continuation of the pulping process, albeit somewhat gentler and less destructive, but bleaching too can degrade cellulose if done improperly.

Lignin imparts a color to the raw pulp (hence its name "brown stock") and unless removed, will continue to darken with age (note the yellowing, darkening, and enbrittlement of newspaper exposed to sunlight). Bleaching by removing the lignin gives higher brightness to the paper than is possible by leaving the lignin in the pulp and brightening by decolorization, and also leads to a more durable and stable paper.

In addition to the removal and decolorization of lignin, bleaching serves to clean the pulp of dirt and foreign matter that escaped the digestion process. Bleaching also removes hemicellulose and extractives (hemicellulose is nearly completely removed for the production of dissolved pulps). Bleaching pulp adds significantly to its value as market pulp because the demand for bleached paper is increasing.

Historical Development of Bleaching Technology

Bleaching of fibers for decolorization has been practiced since early times. Sunlight was one of the earliest bleaching agents. Japanese paper makers were known to bleach fibers by soaking them in water from high mountain streams that contained ozone (the first use of oxygen for bleaching). In 1774, Karl Wilhelm Scheele discovered chlorine and its bleaching action on vegetable fibers. Several years later in 1799, Charles Tennant invented "bleaching powder" (calcium hypochlorite), thereby converting chlorine to an easily transportable form. For the next 130 years it remained the only available bleaching agent. The first time a U.S. paper mill used chlorine for bleaching was in 1804.

Rapid developments in bleaching technology occurred between 1900 and 1930. Multistage bleaching using calcium hypochlorite followed by an alkaline extraction stage, then a repeat of the hypochlorite bleach stage was first adopted by the industry. Later, technologies that allowed the use of gaseous chlorine began to displace hypochlorite in the first bleach stage. The use of chlorine reduced bleaching costs. New equipment developments further improved bleaching efficiency.

Improvements in the manufacture of chlorine dioxide and dioxide bleaching technology were developed in the 1940s. By the 1950s, these developments led to the adoption of the five-stage bleaching sequence that is still used extensively in the industry: (1) chlorine→(2) alkaline extraction→(3) chlorine dioxide→(4) alkaline extraction→(5) chlorine dioxide. The five-stage bleaching sequence allowed very bright pulp to be produced with minor losses in fiber strength.

Oxygen bleaching was discovered in 1952 by V.M. Nikitin and G.L. Akim in the Soviet Union. In the late 1960s, oxygen bleaching was commercialized, followed by the installation of the first displacement bleach plant in the 1970s. This resulted in more rapid bleaching by displacing chemicals through a pulp mat rather than mixing the chemicals

[1]Douglas W. Reeve, "The Principles of Bleaching," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 3.

Box 4-A—What Is Pulp "Brightness"? How Is It Measured?

"Brightness" is the reflecting properties of a sheet of pulp. It is a *physical* and measurable phenomenon. Some mistakenly equate "whiteness" with brightness, but whiteness is a *physiological* phenomenon, measured subjectively by the impression and perception of the human eye. For instance, if blue dye is added to a lightly yellow tinted paper, the sheet will *look* whiter but the sheet will *measure* less reflected light (less brightness).

Since reflectance is affected by the nature and the angle of incident light, the surface properties of the pulp sheet, and other factors, the measurement of brightness has been standardized: Brightness is the reflectance of blue light with a spectral peak at 457 millimicrons from an opaque sample of pulp sheets compared to a specified standard surface.

There are two recognized methods for measuring pulp brightness in North America: 1) the TAPPI method (Technical Association of the Pulp and Paper Industry), Standard T-452; and 2) the CPPA method (Canadian Pulp and Paper Association).

TAPPI Method

Reported in units of *%GE Brightness*. Illuminating light is aimed at 45 degrees to the sample and the reflected light is measured perpendicular to the sample (90 degrees). Reflectance is compared to magnesium oxide powder (98 to 99 percent absolute reflectance). Calibrated opal glass standards are used for routine measurements.

CPPA Method

Reported in units of *ISO Brightness*. The sample is illuminated with diffused light using a highly reflecting integrating sphere. Reflected light measurement is taken at 90 degrees to the sample. Reflectance is compared to absolute reflectance from an imaginary perfectly reflecting, perfectly diffusing surface. Calibrated opal glass standards are used on a routine basis.

A third brightness standard is used throughout the rest of the world: The Zeiss Elrepho standard. It is measured in units termed *Elrepho Brightness*. GE Brightness is measured with a reflectance meter manufactured by the General Electric Corp., while Elrepho Brightness is measured by an instrument manufactured by Zeiss, the German optical company. Since the two meters have different light geometries, there is no simple relationship between the two measurements. In general, Elrepho Brightness is, on average, 0.5 to 1.0 percent higher than GE Brightness.

with the pulp in the conventional way. Since the late 1970s development has taken place in the use of oxygen enrichment in alkaline extraction stages, to further delignify pulp after extended cooking (modifications of the cooking process to improve delignification), and in short bleaching sequences where oxygen is used to supplement chlorine.

Extent of Bleaching in the Industry

Nearly 55 percent of the chemical pulp currently produced in the United States is bleached (table 4-1). By far the greatest proportion of bleached chemical pulp is produced by the kraft process (about 88 percent of the pulp bleached in 1987 was kraft pulp). Very little mechanical pulp has been bleached in the past, however, this is currently changing. Mechanical pulp bleaching is growing at more than twice the rate of chemical pulp bleaching worldwide and it is likely that this trend will continue in the United States as well.[2] Overall, the tendency has been to bleach more pulp as the demand for products using bleached paper increases (nearly 39 percent of the domestic paper and paperboard currently produced is from bleached pulp).

Bleaching Methods

Bleaching Agents

Pulp cooking can safely dissolve up to about 90 percent of the lignin without degrading the cellulose fiber. Additional delignification is done by bleaching. Bleaching of high-yield chemical pulps is achieved by decolorizing with either an oxidizing agent (combines oxygen) or a reducing agent (combines hydrogen). Chlorine gas, sodium hypochlorite, chlorine dioxide, oxygen gas, and hydrogen peroxide are oxidants. Sodium hydrosulfite is a reductant. Alkali is used to remove the solubilized

[2]Ibid., p. 2.

Table 4-1—Domestic Bleached Pulp Capacity
(thousand metric tons)

Grade	1971	1987[a]
Bleached sulfite	1,774	1,256
Bleached kraft	13,364	21,259
Dissolving (bleached)	1,604	1,455
Total chemical pulp produced	32,779	43,800
Percent of chemical pulp bleached	51.1%	54.7%

[a] Estimate
SOURCE: Douglas W. Reeve, "The Principles of Bleaching," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 2.

lignin from the cellulose. Each has its advantages, disadvantages, and limitations (table 4-2).

Since the 1930s, chlorine gas has been the predominant chemical used for the delignification of pulp. Chlorine dioxide can brighten pulp without damaging the cellulose. Oxygen is comparatively inexpensive and is now coming into its own both for delignification (immediately after digestion and before the bleach cycle) and as a supplement in the first extraction (alkali) stage of the bleach sequence. Hydrogen peroxide is expensive, so it is used much less than other bleaching agents. The effectiveness of a bleaching agent, although a major factor in determining its use in a pulp bleaching sequence, may be offset by the cost of the chemical or the equipment needed to handle it.

A critical determinant in choosing a bleaching chemical is the "selectivity" of the agent. Selectivity refers to the capacity of the chemical to attack lignin while doing minimal damage to the cellulose fibers. Unbleached pulp (brown stock) contains high levels of lignin, therefore less selective chemicals (e.g., oxygen and chlorine) can be used in the initial stages of the bleach cycle. With further delignification and lower residual lignin content of the pulp, more chemical is available to react with the cellulose and pulp strength may suffer.

Chlorine dioxide and hydrogen peroxide are highly selective, thus they react rapidly with lignin but affect cellulose very little. The highly selective chemicals are generally used in later bleach stages when the lignin content is low and the cellulose is susceptible to degradation. However, both chemicals are expensive and are therefore used sparingly. Sodium hydrosulfite, a reducing agent, and hydrogen peroxide are used for bleaching lignin-rich mechanical pulp.

Table 4-2—Bleaching Chemicals: Form, Function, Advantages, Disadvantages

Chemicals	Function	Advantages	Disadvantages
Oxidants			
Chlorine	Oxidize and chlorinate lignin	Effective, economical delignification	Can cause loss of pulp strength if used improperly
Hypochlorite	Oxidize, brighten and solubilize lignin	Easy to make and use	Can cause loss of pulp strength if used improperly
Chlorine dioxide	1) Oxidize, brighten and solubilize lignin 2) In small amounts with chlorine gas to protect against degradation of pulp	Achieves high brightness without pulp degradation	Must be made at the mill site
Oxygen	Oxidize and solubilize lignin	Low chemical cost	Used in large amounts. Requires expensive equipment. Can cause loss of pulp strength
Hydrogen peroxide	Oxidize and brighten lignin in chemical and high-yield pulps	Easy to use. Low capital cost	Expensive
Reductant			
Hydrosulfite	Reduce and decolorize lignin in high-yield pulps	Easy to use. Low capital cost	Decomposes readily. Limited brightness gain
Alkali			
Sodium hydroxide	Hydrolize chloroiignin and solubilize lignin	Effective and economical	Darkens pulp

SOURCE: Douglas W. Reeve, "The Principles of Bleaching," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press), p. 6.

Bleaching Sequences

A combination of bleaching and extracting treatments is generally used for bleaching chemical pulps (box 4-B). The bleaching chemicals and the order in which they are used make up the "bleaching sequence." Bleaching sequences generally contain two phases within each sequence: 1) a delignification segment, whose function is to remove the lignin; and 2) a brightening segment, whose principle function is to increase the brightness of the pulp. Examples of delignifaction stages or segments include oxidation by chlorine (C) followed by extraction of the dissolved lignin with sodium hydroxide (E). Brightening segments use sodium hypochlorite (H) and/or chlorine dioxide (D). Oxygen can be used for delignification and for reinforcing extraction of the dissolved lignin in the alkali stage.

Several of the more commonly used bleach sequences in U.S. and Canadian mills are: 1) CEDED, 2) CEDH, 3) CEHDED, 4) CEH, and 5) CED (figure 4-1). Although these are the most prominent bleaching sequences currently in use, an increasing number of mills are now using oxygen in combination with alkali for extraction (E_O), and chlorine dioxide (C_D, D_C) in the chlorination stages. In addition, there are a number of unique bleaching sequences used by some mills (e.g., CEHDH, CEHEDP, CEDPD, $CEDE_HD$, and CEHCHDED).

Box 4-B—Shorthand for Describing Bleaching Sequences

The pulp and paper industry has developed a series of shorthand descriptors for the multistage bleaching sequences. The following abbreviations are used to designate the bleaching agents:

C	Chlorination
E	Extraction with sodium hydroxide
H	Hypochlorite (sodium or calcium)
D	Chlorine dioxide
P	Hydrogen peroxide
O	Oxygen
N	Nitrogen dioxide
Z	Ozone

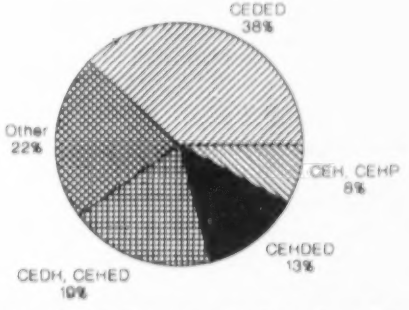
Bleaching sequences are designated by listing each treatment serially. For example, "CEDED" represents a commonly used five-stage bleaching sequence consisting of a first-stage chlorine treatment, followed by a second-stage alkali extraction stage, followed by a third-stage chlorine dioxide treatment, followed by a fourth-stage alkali extraction treatment, and a final fifth-stage chlorine dioxide treatment. Washing is conducted between each chemical application.

Two bleaching agents may be used in a singie stage. For instance, chlorine gas and chlorine dioxide are sometimes combined in an early bleaching stage. If chlorine gas is the predominant agent in the mixture, the treatment would be designated as "C_D." On the other hand, if the mixture contains more chlorine dioxide than chlorine gas, the treatment would be designated as D_C. Other commonly encountered oxidative extraction treatments include E_O (or E/P), E_P, E/H etc.

Factors Affecting the Bleaching Process

Process engineers and paper chemists have a wide range of chemicals, processes, equipment, and operating conditions to choose from in optimizing a bleaching sequence. Cost of chemicals, capital cost of equipment, energy requirements, and other operating costs figure heavily in bleach plant decisions. While cost control is an important factor, the physical and chemical composition of the wood raw material (furnish) and the desired characteristics (brightness and strength) of the finished paper are often more important in selecting bleaching technologies. Bleaching sequences also depend on the pulping process used for initial delignification, some

Figure 4-1—Bleaching Sequences Used in U.S. and Canadian Pulp Mills



SOURCE: Data from David R. Forbes, "Upgrading Existing Bleach Plants," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 116.

of which leave higher residual lignin levels remaining in the brown stock than do others.

The efficiency of the bleach cycle (related to its cost effectiveness), also depends on controlling the operating environment within each bleaching stage. Bleaching is achieved through chemical reactions. Operating conditions are related to temperature, time, chemical concentrations, and degree of acidity or alkalinity (pH).[3] These factors must be kept in balance to achieve the desired degree of bleaching, while at the same time minimizing damage to the cellulose fiber. In addition, the "consistency" (amount of fiber being bleached in relation to the volume of liquid) of the fiber slurry being bleached affects chemical penetration and therefore must also be controlled. Computerization and improved sensors now allow nearly real-time control over the operating environment in all stages of the pulping and bleaching processes.[4]

Lignin Content—Lignin is a large, complex, organic molecule that still holds mysteries for wood chemists. Complete quantitative analysis of lignin from pulp samples would be expensive if performed with precision. This is not necessary from the standpoint of controlling the digestion and bleaching process, however, as simpler methods have been found. Index systems for ranking the lignin content of wood pulp have been devised by the industry (box 4-C).

The lignin content of unbleached pulp, expressed by its kappa number, determines the amount of bleaching required in the bleach sequence to obtain the brightness desired in the finished pulp. The key is to find the optimum point between cooking and bleaching (i.e., the best kappa number for unbleached pulp). For bleachable grades, kappa numbers of unbleached kraft softwood pulp may range between 20 and 40 and hardwood between 15 and 25 as it leaves the digesters in some mills (kappa number 35 represents approximately 5 percent lignin).

Using modern computer-controlled cooking, appropriate chip pretreatment, and chip equalizing systems, it is now possible for well-run kraft mills to produce unbleached softwood pulp consistently with kappa numbers between 28 and 32.[5] Unbleached hardwood pulps can be produced with kappa numbers between 20 and 25.[6] Pulp can be delignified to extremely low kappa numbers (2 to 4) by using chlorination followed by a alkali/oxygen (E_O) extraction stage.[7]

Lignin and Brightness—The lignin content, kappa number, and brightness of chemical pulps are somewhat interrelated. Since pulp brightness is the major objective of bleaching, measurements of brightness expressed as either GE Brightness or as ISO Brightness (see box 4-A) are often used to track progress through the bleaching sequence.

Unbleached kraft pulp has a very low GE Brightness (10 to 20 percent) because of the high absorption of reflected light by the residual lignin.[8] Kraft pulp can be bleached to a very high brightness of 90 percent GE by decreasing its lignin content to near zero without affecting the strength of the pulp. It is possible to bleach kraft pulp to a brightness of 91 to 92 percent GE for special papers.[9] Unbleached acid sulfite pulp with GE brightness of about 60 to 66 percent can also be bleached to 90 percent by removing nearly all of the lignin. Groundwood pulp may have brightness values of about 62 percent GE.

[3]Rudra P. Singh, "Principles of Pulp Bleaching," *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 17.

[4]Thomas J. Boyle and Carr Smith, "Bleach Plant Instrumentation and Computer Control," *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 487 et seq.

[5]Ingemar Croon, Alf de Ruvo, and Gunnar Tamvik, "Bleaching of Kraft Pulps: Oxygen Techniques Today and in the Future," *Svensk Papperstidning No 4*, reprinted by Sunds Defibrator in English (Stockholm, Sweden: Sunds Defibrator, 1985), p. 2.

[6]Kristina Idner, "Oxygen Bleaching of Kraft Pulp—High Consistency vs. Medium Consistency," *1987 International Oxygen Delignification Conference, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 197.

[7]N. Liebergott and B. van Lierop, "Extraction, Part I: Oxidative Extraction," *1987 Bleach Plant Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press), p. 46.

[8]Reeve, op. cit., footnote 1, p. 4.

[9]W. Howard Rapson and Gene B. Stumila, "Chlorine Dioxide Bleaching," *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 142.

Box 4-C—Assessing Lignin Content and Pulp Bleachability

The Technical Association of the Pulp and Paper Industry (TAPPI) has devised two standardized procedures for determining and reporting the lignin content of pulp: 1) Permanganate (K) number (TAPPI Test Method T214), and 2) Kappa number (TAPPI Test Method T236). These indices are used by the industry to control cooking within the digester during pulping and for determining the bleachability of the pulp.

Both methods are chlorine demand tests and are based on the amount of permanganate needed to oxidize the contained lignin. The Permanganate, or K number, is used for determining the bleachability of chemical pulps having lignin contents below 6 percent (based on weight of oven-dry pulp). The kappa number is applicable to all grades of chemical and semi-chemical wood pulps, including higher lignin content pulps with yields as high as 70 percent.

Standard procedures have been established for both bleaching indices. Both are based on the amount of potassium permanganate that can react with dry pulp samples. Most modern pulp mills now use automated, continuous oxidation-reduction measurements or optical devices such as brightness meters for on-line measurements to gauge the progress of delignification and the need for additional bleaching. However, permanganate tests are still used in mill laboratories for verification of the instrument reading.

Bleaching Systems

Bleaching sequences apply various bleaching agents in different orders and combinations. Between each bleaching stage the pulp is generally (but not always) flushed with an alkali extraction solution to remove the dissolved lignin before it is sent to the next bleaching stage (figure 4-2). The first step of a bleaching sequence is designed to remove the bulk of the residual lignin (delignification) and involves little or no improvement in the brightness of the pulp (figure 4-3). This step, along with the following extraction stage, is called "prebleaching." The purpose of prebleaching is to remove as much lignin from the pulp as possible to minimize the volume of more expensive bleaching chemicals (e.g., chlorine dioxide, hypochlorite, and hydrogen peroxide) needed in subsequent bleaching stages.

Chlorine gas and sodium hydroxide (CE) have been the preferred chemicals for the prebleach stage of the bleaching process. More recently, mixtures of chlorine and chlorine dioxide have been used in place of (or in addition to) pure chlorine treatment (table 4-3).[10] Other prebleaching processes are slowly displacing CE as the first stages of the bleach sequence at some mills. Prebleach oxygen delignification and extended cooking may shorten the bleaching sequence by reducing the amount of lignin carried forward to the bleaching process.[11]

Impetus for considering alternatives to the conventional CE stage are based partially on reducing the cost of bleach plant operations and partially on concerns about environmental impacts from discharged bleaching effluents. These concerns result from detection of chlorinated organic material containing chloroform and dioxins in bleached pulp mill sludge. Most of the chlorinated organics contained in bleach plant effluent originate from the first chlorine, alkaline extraction, and hypochlorite stages.

Brightening stages that follow prebleaching remove less lignin but bring out the brilliance of the pulp through bleaching action. The brighter the pulp desired, the more bleaching stages that must be used (table 4-2). Mill operators have a number of mix-and-match brightening processes to chose from for final bleaching. Choices are largely determined by the relative costs and efficiencies of the bleach options and the required brightness of the pulp being produced. The entire bleaching sequence is then a combination of the prebleaching stages and the brightening stages.

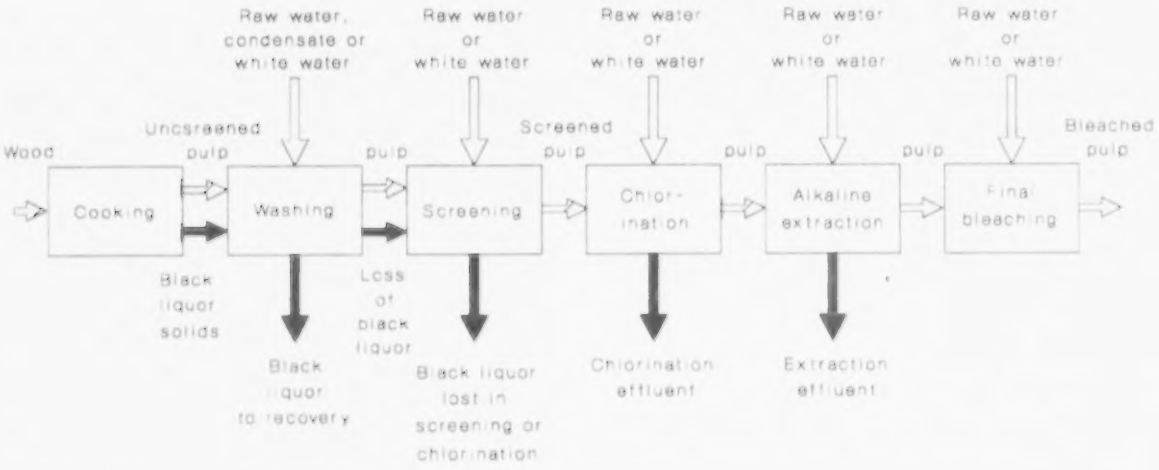
Prebleach Delignification

Chlorination—Chlorine selectively reacts with lignin and under normal bleaching conditions does little harm to cellulose fibers. Because of its relative

[10]Rudra P. Singh and Edward S. Atkinson, "The Alkaline Extraction," *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 89.

[11]Johan Gullichsen, "The Past and Future of Pulp Bleaching," *1987 Bleach Plant Operations Seminar, TAAPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 19.

Figure 4-2—Sequence for the Production of Fully Bleached Chemical Pulp



SOURCE: Carlton W. Dence and Goran E. Annergren, "Chlornation," *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 51.

cheapness in comparison with other bleach chemicals it became widely used for delignification after the pulping process. Chlorination in the prebleach cycle begins with washed brown stock pulp slurry at low consistency (3 to 5 percent weight of pulp to water) being pumped into a chlorination mixer. Chlorine gas, which is often dispersed in water, is added to the pulp slurry in the mixer and is vigorously mixed (figure 4-4).

The reaction between chlorine and lignin begins immediately in the mixer, and the reaction is completed in a chlorination tower designed to give the proper retention time. If chlorination is conducted at low temperatures (5 to 45 °C) retention time may range between 15 and 60 minutes. Higher temperatures reduce the time necessary to complete the chemical reaction. The chlorinated pulp is washed before being sent to the alkali extraction stage.

Chlorination is sometimes repeated after extraction if additional delignification is needed, but because of possible cellulose damage a chlorine dioxide stage is often used. Throughout the process brightness, kappa number, and other indicators of pulp quality are monitored.[12]

There is a trend toward modification of the first chlorination stage by including other bleaching agents (e.g., chlorine dioxide, with the chlorine charge). Inclusion of these chemicals can reduce cellulose degradation, improve pulp strength, and reduce environmental releases. Chlorine dioxide is sometimes used sequentially preceding the chlorine treatment and has been shown to be more effective than when the two chemicals are mixed.[13] Chlorine dioxide can be used to completely replace chlorine in the first delignification stage, but its gains in pulp quality do not offset the additional expense, and pulp brightness equivalent to that produced by chlorine can not be achieved.[14] Pretreatment with sodium hypochlorite prior to chlorination has improved the delignification of resinous woods.

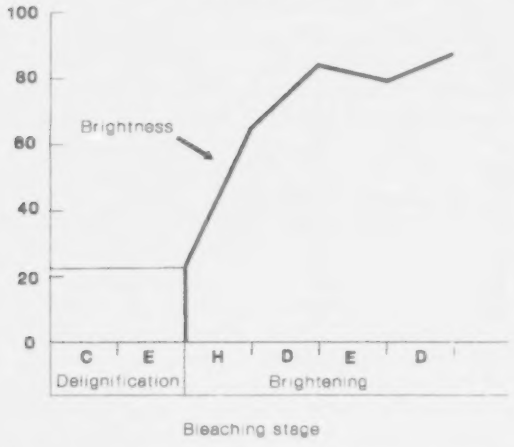
Alkaline Extraction—Hot alkaline extraction is the second stage in the pulp bleaching process and completes the prebleaching delignification process.

[12]Douglas W. Reeve, "Pulp Chlorination," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 37.

[13]Carlton W. Dence and Goran E. Annergren, "Chlorination," *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 65.

[14]Douglas C. Pryke, "Chlorine Dioxide in the Chlorination Stage," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 55.

Figure 4-3—Pulp Brightness at Stages of the Bleaching Sequence CEHDED



SOURCE: N. Liergott and B. Van Lierop, "Oxidative Bleaching A Review: Part I: Delignification," *Pulp & Paper Canada*, vol. 87, No. 8, 1986, p. 58.

Table 4-3—Examples of Prebleaching Sequences for Pulp Delignification

CE	Chlorine – Alkali extraction
C_DE	(Chlorine + Chlorine dioxide) – Alkali extraction
CE_O	Chlorine – (Alkali + Oxygen extraction)
OC_DE	Oxygen – (Chlorine + Chlorine dioxide) – Alkali extraction
DCE	Chlorine dioxide – Chlorine – Alkali extraction

SOURCE: Douglas W. Reeve, "The Principles of Bleaching," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 10.

Moderate temperature or cold temperature alkaline extraction is also used after later bleach stages in the brightening process of multistage bleaching sequences. Cold alkaline extraction is particularly important in the production of dissolving pulps for the manufacture of rayon and acetate. Alkaline extraction removes the soluble colored components and lignin released in the preceding delignification stage (chlorination or oxygen), therefore reducing the amount of bleaching chemicals needed in subsequent stages and improving the durability of the pulp.

Sodium hydroxide has been shown to be the most efficient alkali for decreasing the kappa number of pulp. Efficient extraction is nearly as important as prebleach delignification in the first bleaching stage. For instance, after chlorination and washing, but before alkaline extraction, about 30 to 50 percent of the chlorinated lignin in removed. After alkaline extraction, 80 to 90 percent of the lignin is removed.[15] A second hot alkaline extraction is sometimes used later in the bleach sequence after bleaching with chlorine dioxide or sodium hypochorite (e.g., CEHED, CEHDED, or CEDED sequences) to improve pulp brightness stability and conserve bleach chemicals.[16]

The pulp is subjected to the alkaline extraction treatment for 60 to 90 minutes at most mills in the first post-chlorination extraction stage, although some operate on a shorter schedule. The second alkaline extraction usually lasts from 30 to 60 minutes.

The first alkaline extraction stage contributes the largest potential pollutant load released from the pulp bleach plant. It may be possible to reduce the pollutant loss from the extraction stage considerably by substituting oxidative extraction, particularly sodium hypochlorite, for the first alkaline extraction stage (e.g., CHED, bleaching sequences).[17] Sodium hypochlorite added to the sodium hydroxide extraction solution (E_H) may reduce the color (a rough indicator of pollution load) in waste water by about one-half.[18] Even larger reductions in waste water color (about three-quarters) have resulted when hydrogen peroxide is added at the alkaline extraction stage.

Oxidative Extraction—Oxygen gas added to sodium hydroxide in the extraction stage (E_O) decreases the kappa number, conserves chemicals in subsequent bleaching stages (in some cases it can reduce the number of bleaching stages), and reduces pulp strength loss and coloration in the waste water.[19] Studies have shown that the addition of

[15]B. van Lierop et al., "Caustic Extraction, Part I: Reaction Variables," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 44.

[16]Singh and Atkinson, op. cit., footnote 10, p. 91.

[17]Ibid., p. 99

[18]Liebergott and van Lierop, op. cit., footnote 7, p. 46.

[19]Ibid., p. 47.

other oxidizers, such as hydrogen peroxide or sodium hypochorite, to an E_O extraction stage might allow for a shortened, three-stage bleaching sequence capable of bleaching pulp to high brightness (88 to 90 percent ISO). The E_O extraction stage has gained rapid acceptance since only modest additional investment in new equipment is needed.

Oxygen has been substituted for alkaline extraction immediately after the chlorination stage.[20] If coupled with a following chlorine dioxide bleach stage, the COD sequence can produce fully bleached pulp with major savings in chemicals. A three-stage sequence using oxygen in the second stage following a chlorine dioxide-chlorine delignification stage ((DC)OD) has been used by the Chesapeake Corp. at West Point, Virginia since 1972. The Chesapeake mill was the first commercial application of oxygen in the extraction stage.

Table 4-4—Common Sequences Used To Bleach Kraft Pulp to Various Degrees of Brightness

Range of GE% brightness	Sequence
70-80	CEH
	CEHH
	CHEH
80-85	CEHEH
	CC_HEHH
	CED
	CEHD
85-92	CHED
	CEHDD
	CC_HED_H
	CEDED
	CEDHED
	C_DE_QDED
	OC_DEHD

SOURCE: Adapted from Allan M. Springer, *Industrial Environmental Control: Pulp and Paper Industry* (New York, NY: John Wiley & Sons, 1986), p. 161.

Brightening Stages

Chlorine Dioxide—Chlorine dioxide is very selective in attacking lignin without significantly degrading cellulose, while producing high brightness pulp. In the dioxide bleach stage, chlorine dioxide is generated as a gas at the mill and dissolved in cold water. The aqueous chlorine dioxide solution is mixed with the prebleached pulp, heated to about 70 °C, and is normally held in a reaction vessel for approximately 3 hours.[21]

Because of chlorine dioxide's high cost, it is most commonly used at or near the end of bleaching sequences (e.g., CEHD, CEHED, CEDED, and CEHDED). Sequences using chlorine dioxide in only one bleach stage generally produce lower brightness pulps.[22] For instance, the CEHD sequence on softwood kraft pulp would probably be limited to 85 percent G.E. brightness. In order to achieve the highest brightness (90+ percent G.E.), two chlorine dioxide stages are generally required (e.g., CEDED and CEHDED sequences). Chlorine dioxide can also be used in conjunction with a hydrogen peroxide bleach stage (CEHDP or CEDPD) to produce 90+ percent G.E. brightness pulp.[23]

Peroxide—Hydrogen peroxide is a very effective cellulose-preserving bleach agent and is well suited for improving the brightness of highly lignified pulps, such as mechanical groundwood or chemimechanical pulps, without significantly reducing its yield. Hydrogen peroxide is an extremely versatile delignifying chemical and has been proposed for use as a chip pretreatment before kraft pulping and as a delignifier in the prebleach stage prior to, or as a substitute for, the C, C_D, or D_C prebleaching stages.[24] It is also used in association with sodium hydroxide in alkaline extraction (E_P) Because of its high cost, hydrogen peroxide is used most often in the later stages of pulp bleaching.

Peroxide is used in the intermediate stages of the bleaching sequence as a replacement for hypochlorite or chlorine dioxide. It is frequently used as the last stage in the bleach sequence where it can add a few points of brightness to the pulp and improve its brightness stability. Peroxide alone is a relatively

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[20] P. Singh and Bjorn C. Dillner, "Oxygen Bleaching," *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 181.

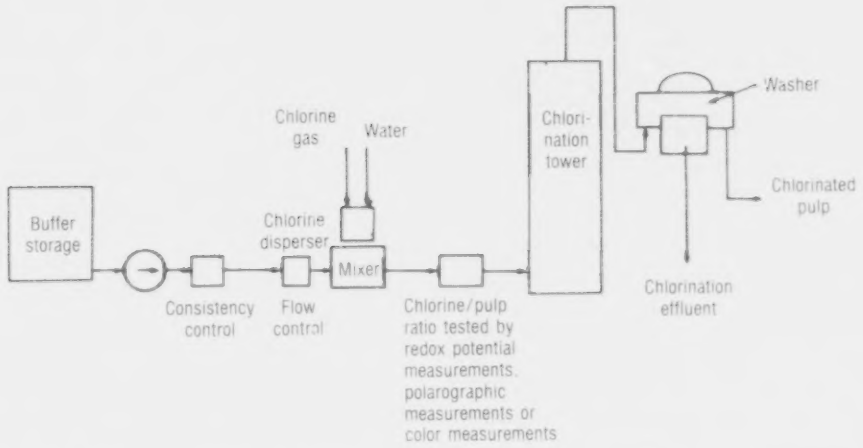
[21] on and Strumila, op. cit., footnote 8, p. 114.

[22] Douglas W. Reeve, "Chlorine Dioxide Bleaching," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 198 67.

[23] Rapson and Strumila, op. cit., p. 144.

[24] J.R. Presley and R.R. Kindron, "Hydrogen Peroxide Bleaching," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 75.

Figure 4-4—Schematic Diagram of the Chlorination Process



SOURCE: Carlton W. Dence and Goran E. Annergren, "Chlorination," *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 52.

ineffective means for bleaching kraft pulp.[25] However, when used in sequences with chlorine-based bleaching agents, peroxide is an efficient delignifier and brightner. Peroxide is also used for intermediate bleaching stages of the kraft bleaching sequence or as a final treatment to increase and stabilize the brightness of chemical pulps.[26]

The peroxide bleach liquor is usually in the range of 1 to 3 percent hydrogen peroxide. An appropriate volume of peroxide liquor, sodium hydroxide, and other chemicals to stabilize the peroxide are mixed with pulp and heated with steam to the reaction temperature (35 to 70 °C). The peroxide-pulp mixture is allowed to react under controlled temperature for an optimum time (1 to 5 hours). When the reaction is complete, the pulp is washed and sent to the next bleaching stage or washed and neutralized with sulfur dioxide if it is the final bleach stage.

Peroxide, coupled with oxygen and/or ozone, shows some promise in research laboratory evaluations for formulating chlorine-free bleach sequences to reduce release of chlorinated organics in the waste stream. A three-stage sequence OZP (oxygen, ozone, peroxide) has yielded brightness values of 85 percent GE in euchalyptus kraft pulp.[27] However, the pulp suffered a substantial loss in tear strength. The ZP bleaching sequence produced southern pine oxygen pulps of 80 percent GE brightness with good brightness stability. In contrast to peroxide and oxygen bleaching, ozone bleaching has not been developed to the point of commercialization.

Hypochlorite—The use of hypochlorites for bleaching wood pulp began in the early 1880s. Although the development of chlorine bleaching technology in the 1900s led to a decrease in the use of sodium and calcium hypochlorite, still about 40 percent of the kraft pulp mills in the United States and Canada use at least one hypochlorite stage in their bleach sequence. Hypochlorites have been used effectively on sulfite pulps where an alkaline extraction stage is interposed with two hypochlorite stages (HEH).[28]

[25]D.H. Andrews and R.P. Singh, "Peroxide Bleaching," *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI Press, 1987), p. 237.

[26]Ibid., p. 212.

[27]Ibid., p. 243.

[28]Lee E. Larsen and H. deV. Partridge, "Bleaching With Hypochlorites," *The Bleaching of Pulp, Third Editions* (Altanta, GA: TAPPI Press, 1979), p. 101.

Kraft pulps, being more difficult to bleach than sulfite pulps, require that a chlorine and alkaline extraction stage be added in the prebleach segment of the bleach sequence. Until chlorine dioxide and peroxides became available in the 1940s, kraft pulps of 85 percent GE brightness were the brightest that could be produced with hypochlorite bleaching and still maintain acceptable pulp strength, but these pulps had poor brightness stability.

Hypochlorite is nonspecific, that is, it attacks cellulose as well as lignin, therefore it requires careful control if a reduction in pulp strength is to be avoided.[29] Bleaching sequences such as CEHD, CEHED, and CEHHD are used widely for producing pulps of 86 to 88 percent GE brightness, CEHDED is used for pulps of 88 to 90+ percent GE brightness, and CEHDP and CEHEDP for pulps of 90 percent GE brightness using peroxides. Hypochlorite is also used in small amounts for oxidative extraction (see above). Some mills use hypochlorite as a replacement for the first alkaline extraction stage to reduce the color in bleach plant effluent.[30]

Retention times and chemical concentrations vary for hypochlorite bleaching depending on which stage it is being used in the bleaching sequence. Retention times range from a low of 30 minutes at some mills to 3.5 hours for those using hypochlorite in the brightening stage. Reaction temperatures for hypochlorite stages are generally kept low (85 to 110 °F) to minimize cellulose degradation.

A "simplified bleaching" process for hypochlorite has recently been developed.[31] Simplified bleaching uses a short (10-minute) bleach cycle at higher temperatures than normally used (180 °F). The hypochlorite treated pulp is sent without washing to a chlorine dioxide stage. This ostensibly produces pulps of higher brightness at lower cost.

Studies have shown that one of the largest contributors to the environmental release of chloroforms from a bleach plant is the effluent from the hypochlorite stage.[32] It is hypothesized that chloroform is produced under specific conditions existing in the hypochlorite stage rather than simply as the result of chlorine-based chemicals. The specific conditions and reactions contributing to the production of chloroform are not well known, however, and more research is needed to establish causation. These early findings of the linkage between hypochlorite reactions and chloroform production has led some to propose that the release of chloroform compounds from pulp mills could be reduced by eliminating the large-scale use of hypochlorite in the bleach sequence.

Ozone—Ozone is one of the most powerful bleaching and oxidizing agents. It is a special form of oxygen produced by the discharge of an electrical current in oxygen gas. While oxygen atoms normally occur in pairs, the electrical discharge makes three atoms associate with one another, thus giving extraordinary oxidative properties to ozone. Its decomposition to oxygen after bleaching produces neither a residue, nor undesirable inorganic byproducts. Ozone, in a bleaching sequence with hydrogen peroxide, can produce high-brightness pulps. Ozone is not used commercially for pulp bleaching. Some pilot plant studies have been conducted, but additional development work would be needed to permit its widespread commercial use.

Ozone, in conjunction with preliminary oxygen delignification, holds promise for reducing the amount of chlorine and hypochlorite used in the prebleach and brightening stages of the bleaching sequence. Ozone bleaching is particularly well suited to bleaching sulfite pulps because of their low residual lignin content.[33] High-brightness, high-quality, hardwood kraft pulps can be produced by using ozone in the first stage of the bleaching

[29]E.B. Althouse, J.H. Bostwick, and D.K. Jain, "Using Hydrogen Peroxide and Oxygen to Replace Sodium Hypochlorite in Chemical Pulp Bleaching," *TAPPI J.*, vol. 70, No. 6, June, 1987, p. 113.

[30]Larsen and Partridge, op. cit., p. 102.

[31]R.G. Hise and H.L. Hintz, "Hypochlorite Bleaching," *1987 Bleach Plant Operations Seminar, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1987), p. 65.

[32]Ibid.

[33]R. Patt et al., "Laboratory and Pilot Plant Bleaching of Various Pulps With Ozone," *1984 Oxygen Delignification Symposium, TAPPI Notes* (Atlanta, GA: TAPPI Press, 1984), p. 33.

sequence (e.g., ZEP, ZEZP, and ZED).[34] Because it is a very powerful and nonselective chemical, its use is usually limited to the early bleaching stages.

Kraft softwood pulps must be delignified, preferably with oxygen or through extended cooking to reduce the need for chlorination in the prebleach segment, before bleaching with ozone. Low kappa number kraft softwood pulps bleached with the OZEP sequence produced pulp comparable in brightness and strength to those produced from the CEHED five-stage sequence.[35] Brighter kraft softwood pulp can be produced with oxygen-ozone-peroxide and/or chlorine dioxide bleaching sequences (e.g., OZEP, OZE_pP, OZEPD, OZED, and OZE_pD). For the highest brightness, chlorine dioxide was needed in the final bleaching stage.

Ozone is not currently used commercially by the industry. Experimental results and pilot plant operations indicate that ozone might have future promise as an alternative bleaching agent. Further discussion of oxygen-based, nonchlorine bleaching technology, including ozone bleaching, is found in chapter 5.

[34]Steven S.K. Ow and Rudra P. Singh, "Advances in Ozone Bleaching, Part II: Bleaching of Softwood Kraft Pulps With Oxygen & Ozone Combination," *Oxygen Delignification Syposium JAPPI Notes* (Atlanta, GA: TAPPI Press, 1984), p. 43.

[35]Ibid., p. 49.

Chapter 5

Technologies for Reducing Chlorinated Organics in Pulp Manufacture

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Chapter 5

Technologies for Reducing Chlorinated Organics in Pulp Manufacture

The bleaching plant is the major source of waterborne environmental pollutants produced by pulp and paper mills. As much as 40 percent of the biological oxygen demand (BOD), 25 percent of the suspended solids (SS), 70 percent of the color, and nearly all of chlorinated organic materials (TOCl) produced by pulp mills originate in the bleaching process. The amount and nature of bleach plant pollutants vary considerably among the bleaching sequences used, wood species, and pulping processes.

Water is used in large quantities in the bleaching process (averaging 20,000 to 30,000 gallons per ton of pulp produced, although modern mills use much less than this). In contrast to pulping chemicals, the bleaching chemicals are generally not recovered but are discharged as wastes after treatment.

Chlorination, often the first bleaching stage after pulping in many bleaching sequences, requires large volumes of water to dilute the unbleached pulp to a low consistency for subsequent bleaching (about 3 percent fiber by weight compared to water), and is therefore a major source of chlorine-contaminated water. Chlorination sometimes uses as much water as all of the subsequent bleaching stages combined. To reduce the amount of fresh water consumed, the chlorination filtrate is often recycled in the bleaching stage, or paper mill white water is used for dilution.

General hypotheses have been advanced to explain the possible occurrence of dioxins in pulp, paper, and mill wastes. If true, these hypotheses may suggest ways to reduce the amount of dioxins produced in pulp and paper manufacture. First, since lignin or wood extracts probably contain some dioxin precursors, the reduction of the amount of lignin exposed to chlorine in the bleach plant might reduce the volume available for dioxin formation. It is now believed that lignin may not be a major source of precursors as originally thought.

Second, by reducing the amount of chlorine used, or eliminating the use of chlorine bleach altogether, the formation of dioxins might be reduced or even eliminated.

Third, a recent discovery by the Pulp and Paper Institute of Canada that oil-based defoamers made with contaminated used oil may be the source of nonchlorinated precursors of dioxin and furan that become tetrachloro-p-dibenzodioxin (TCDD) and tetrachlorodibenzofuran (TCDF) with chlorination.[1] By using "cleaner" oil- or water-based defoamers (although water-based defoamers may not be effective in washing brownstock), this source of precursors can be eliminated.

Fourth, preliminary findings indicate that the formation of TCDD and TCDF can be reduced by modifying conventional chlorine bleach sequences. For instance, by applying chlorine gas in smaller, successive split charges rather than a single large charge, research has shown reductions in TCDD.[2] By carefully controlling the acidity (pH) of the unbleached pulp within an optimum range, TCDD has also been reduced. Applying chlorine bleach before the addition of chlorine dioxide (CD) tends to produce less TCDD than if chlorine and chlorine dioxide are mixed (C_D) or if chlorine dioxide is applied separately before the addition of chlorine. TCDD and TCDF formation is also sensitive to the ratio of chlorine to lignin. The Swedish Pulp and Paper Research Institute has found that if chlorine additions are kept below 15 percent (chlorine to lignin), TCDD and TCDF can be kept to low levels.[3] These observations need verification.

Fifth, improvements in secondary biological waste treatment can further reduce the amount of fine, colloidal suspended solids on which TCDD and

[1]R.H. Voss et al., "Some New Insights Into the Origins of Dioxins Formed During Chemical Pulp Bleaching," *Canadian Pulp and Paper Association Environment Conference Proceedings*, Vancouver, B.C., Oct. 25-26, 1988, p. 31.

[2]Ronald B. Estridge and William Kraske, American Paper Institute, material presented at the OTA dioxin workshop, Washington, DC, Nov. 14-15, 1988.

[3]Knut P. Kringstad et al., "Bleaching and the Environment," *1988 Pulp Bleaching Conference*, Orlando, FL, June 5-9, 1988 (Atlanta, GA: TAPPI, 1988).

TCDF are transported.[4] Supplemental treatment with chemical coagulants, precipitants, adsorbents, and perhaps destruction by ultraviolet light and chemicals could increase the efficiency of the existing waste treatment facilities. Further evaluation is needed on these options.

Should it prove necessary to reduce the amount of dioxins produced from pulp and paper manufacture for health or environmental reasons, one approach to consider is prebleaching technologies that would reduce the amount of lignin passing to the bleach plant. Another approach would utilize brightening technologies that reduce or eliminate chlorine gas from the bleaching sequence. The several options available to reduce the formation of TCDD, TCDF, and other chlorinated organics are not mutually exclusive and can be linked at stages throughout the pulping, bleaching, and waste disposal processes to achieve low levels of discharge.

Because of the pollution potential of chlorinated compounds and the volume of wastewater produced by chlorine bleaching, the chlorination stage is the focal point for efforts to control pollution resulting from the manufacture of pulp. There are several possible approaches to reducing the amount of dioxin and other chlorinated organics formed during chlorine bleaching:

- Delignify pulp to a further degree before bleaching
  - —extended delignification
  - —oxygen delignification
  - —pretreatment with nitrogen (more lignin can be removed without fiber damage)
- Substitute other bleaching chemicals for chlorine
  - —chlorine dioxide for part or all of the chlorine
  - —hydrogen peroxide
  - —alkaline extraction supplemented with oxygen and peroxide
  - —ozone (precommercial)
- Modify chlorination procedures (more research needed)
  - —optimize the acidity (pH) of the pulp
  - —use smaller multiple charges of chlorine instead of one
  - —apply chlorine first, then bleach with chlorine dioxide
- Remove known sources of precursors (e.g., contaminated defoamers or other additives, prewash pulp, etc.)
- Improve waste treatment systems (more research needed)
  - —chemical coagulants
  - —sorption or precipitation enhancers
  - —destruction with ultraviolet light or chemicals
  - —anaerobic treatment

Elimination of chlorine in the bleach sequence combined with internal recycling of process water aimed at developing an overall "pollution free" pulping system probably offers the best theoretical strategy for reducing the pollution from bleach plants over the long term, but because of practical limitations, it may not be commercially viable for sometime.[5]

OXYGEN DELIGNIFICATION

Although the introduction of any chlorinated bleaching chemical (e.g., chlorine gas, sodium, or calcium hypochlorite), can generate some chlorinated organic compounds, chlorine gas used in the prebleaching stages of the bleaching sequence produces the largest amount (figure 5-1). Chlorinated organics produced by pulp mills contain small amounts of TCDD and TCDF (see ch. 2).[6] Their presence in pulp mill wastes is ascribed to chlorination in the bleach sequence although the precise chemical reactions and mechanisms that produce dioxins are not known. Other factors might also contribute to dioxin formation.

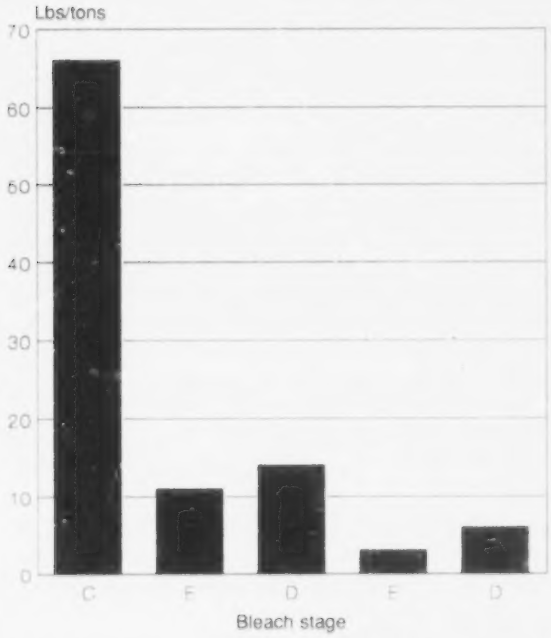
Ever since the connection was made between dioxin and the use of chlorine, the emphasis of those advocating process changes to reduce the formation of TCDD, TCDF, and other chlorinated organics has focused on oxygen delignification technology. The Swedish example has served as a demonstration of

[4]U.S. Environmental Protection Agency, *USEPA Bench Scale Wastewater Treatability Study Pulp and Paper Mill Discharges of 2378-TCDD and 2378-TCDF: Proposed Interim Control Measures Interim NPDES Permit Strategy* (Westlake, OH: EPA Region 5, 1988), p. 17.

[5]Allan M. Springer, *Industrial Environmental Control: Pulp and Paper Industry* (New York, NY: John Wiley & Sons, 1986), p. 161.

[6]U.S. Environmental Protection Agency, *National Dioxin Study*, EPA/350-SW-87-025, August 1987, p. III-33.

Figure 5-1—Chlorinated Waste From Bleaching of Hardwood Pulp



SOURCE: Allan M. Springer, *Industrial Environmental Control: Pulp and Paper Industry* (New York, NY: John Wiley & Sons, 1986), p. 166.

one method to reduce the amount of chlorine needed in the bleaching process. Sweden has encouraged the international move toward adopting oxygen delignification to solve the chlorine problem. It should not be overlooked that first, most of the bleached kraft mills in Sweden have already installed oxygen delignification at a considerable capital expense, and second, oxygen delignification is a Swedish technology largely manufactured in Sweden.

The effectiveness of oxygen delignification to reduce the amount of chlorine needed is well documented. It should be noted, however, that other technologies and process modifications are also available that can reduce the amount of dioxins produced, but none will reduce the amount of chlorine-based bleach needed to the degree that oxygen can. Conversion to oxygen delignification is not always the best solution. However, the substitution of oxygen bleaching for chlorination in prebleaching and brightening sequences is considered by some pulp and paper experts to be a technological trend that likely defines the future state-of-the-art in low-chlorine bleach plant design.

Effluent from oxygen bleaches, such as oxygen gas, ozone, or peroxides, can be recycled internally to destroy harmful byproducts that might be formed. Transition from conventional chlorine bleaching to oxygen delignification and bleaching has been faster in Scandinavian countries—particularly Sweden—than it has in the United States and Canada.[7] In Sweden, oxygen bleaching has been used in place of biological waste treatment that is commonly used in North America. Although oxygen delignification was developed in the Soviet Union, the process was commercialized in Sweden in the late 1960s and in the Union of South Africa in the early 1970s.

Early interest in oxygen delignification stemmed primarily from its ability to reduce pulp mill pollution. Substantial reductions in BOD, color, and chlorinated organics in the effluent can be realized, as well as savings in bleaching agents. Oxygen prebleaching may not significantly alter the kinds of chemicals formed (although this has not been determined with certainty), but, when properly conducted, it will probably generate smaller quantities of all these compounds.[8] Moreover, bleaching operations using oxygen do not normally call for a hypochlorite stage, as a result, little chloroform is released (other non-oxygen bleaching sequences also do not use hypochlorite stages, e.g., CEDED).

Chlorinated organics—not specifically dioxins—are major pollutants in the Baltic Sea. Nowhere in the United States have chlorinated organics presented the problems that have been experienced in the Baltic region. BOD has been the major environmental concern in the United States (U.S. standards for BOD were stricter than Sweden's); attempts to

[7]Fifteen Swedish pulp mills manufacture bleached sulfate pulp. Nine mills currently use oxygen in the first prebleaching stage of the bleaching sequence and two others have plans to install oxygen stages in the bleach sequence. Committee for the Gulf of Bothnia, Water Pollution Problems of Pulp and Paper Industries in Finland and Sweden, Naturvardsverket Rapport 3384, May 1987, p. 55.

[8]Knut Kringstad and Krister Lindstrom, "Spent Liquors From Pulp Bleaching," *Environmental Science and Technology*, vol. 18, No. 8, 1984, p. 246A.

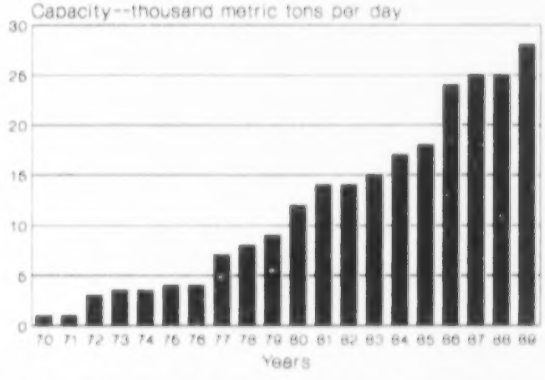
address this problem have relied on secondary biological waste treatment and internal changes in pulp mill processes.

With the exception of Sweden and Germany (Germany has no kraft mills), where environmental requirements have forced acceptance, economics have been a significant motivating factor in adoption of oxygen delignification technology. For instance, in Japan where oxygen delignification systems have recently gained acceptance, oxygen is cheap because it is produced as a byproduct of nitrogen recovery, which is needed in the manufacture of printed electronic circuits. At North American mills where oxygen delignification has been installed, waste improvements have been accompanied by economic benefits from shorter bleaching sequences and smaller and cheaper effluent treatment systems.

Oxygen delignification can cause degradation of the pulp and reduce paper strength. In 1963, this problem was reduced with the discovery that the addition of magnesium chemicals (e.g., magnesium carbonate or sulfate) can reduce or prevent degradation of cellulose fibers.[9] Oxygen delignification and bleaching produces pulp that compares favorably with conventional bleached pulps in most ways. Strength properties of oxygen pulps are slightly less than conventional pulps, but may be acceptable for some products if delignification by oxygen does not exceed about 40 to 50 percent of the pretreatment lignin level.[10] Experts differ as to the viscosity and strength of oxygen pulp compared to conventional pulp. Brightness stability for oxygen pulps is equal to or better than that of conventional pulps.

Since the construction of the first pulp mill to use oxygen delignification in 1970 at Enstra, South Africa, there has been a steady increase in the annual world production of oxygen pulps (figure 5-2). In 1988, world installed capacity was expected to exceed 10 million metric tons per year. About half the oxygen capacity is in Scandanavia and Europe, one-fifth is in North America, and one-fifth is in Japan. About 92 percent of the installed capacity of oxygen delignification systems is in kraft mills, and 60 percent is in bleached softwoods (table 5-1). The use of oxygen delignification is expected to expand worldwide as environmental standards are tightened and will likely accelerate even more if savings in the cost of bleach plant operations favor oxygen pulps.

Figure 5-2—World Production Capacity of Oxygen-Delignified Pulp



SOURCE: Larry Tench and Stuart Harper, "Oxygen Bleaching Practices and Benefits: An Overview," *TAPPI Journal*, November 1987, p. 57.

Capital cost of oxygen delignification systems is high. Cost estimates based on prior conversions from a conventional chlorine bleaching process to oxygen delignification range between $20 million and $30 million for an existing pulp mill with a capacity of 750 to 1,000 tons per day, depending on the need to modify supporting equipment, such as recovery boilers, evaporators, etc. If the mill required expansion of supporting equipment, such as evaporators and brownstock washers, the cost would escalate to $40 million to $50 million. If, in addition, the mill did not have sufficient reserve recovery boiler capacity, the additional liquor treatment required for oxygen delignification would raise the cost to $80 million. However, if the mill did not require recovery modifications, costs may go as low as $8 million to $10 million.

The American Paper Institute estimates that if the 98 bleached chemical pulp mills in the United States that have not yet installed oxygen delignification equipment (5 have already done so for a combined

[9]I. Croon and D.H. Andrews, "Advances in Oxygen Bleaching: I. Demonstration of Its Feasibility and Scope," *TAPPI Journal*, vol. 54, No. 2, p. 1893 *et seq*.

[10]Larry Tench and Stuart Harper, "Oxygen-Bleaching Practices and Benefits: An Overview," *TAPPI Journal*, November 1987, p. 55.

total of 6,100 tons per day of oxygen pulp capacity). The total capital outlay to the U.S. industry would then be about $3 billion or $40,000 per daily ton of capacity to fit out the U.S. industry with oxygen systems (if capital costs were annualized and changes in operating costs were considered, the costs of oxygen delignification would be lower).

For greenfield construction of a new bleached chemical pulp mill using oxygen delignification, the capital cost of an oxygen system is more attractive. The capital cost of installing an oxygen delignification system in a mill of 1,000 tons per day capacity could be between $25 million to $35 million more than for conventional chlorine bleaching. The higher cost of oxygen delignification compared to conventional chlorine bleaching is part due to the cost of the oxygen generating plant ($12 million to $14 million), and part due to the need for larger recovery boilers.[11]

Oxygen Delignification Technology

The objective of chemical pulping is to reduce the amount of lignin carried forward with the brownstock pulp to the brightening stages of the bleach plant. The less lignin that prebleached pulp contains, the less bleaching that is required. Conventional kraft pulping, for example, produces pulp with a kappa number between 32 and 35. By subjecting conventional pulp to oxygen delignification, the kappa number may be reduced to 16 or 17.[12] This allows the use of a short bleaching sequence, since the amount of lignin to be bleached is reduced up to 50 percent. An even higher proportion of lignin can be removed from sulfite pulp. Oxygen delignification is considered to be an extension of the cooking process. With an oxygen bleached pulp it is possible to reduce the amount of chlorine gas bleach. With additional research and development, it may be possible to eliminate it altogether by using ozone, hydrogen peroxide, and/or chlorine dioxide.

Effluent from the oxygen delignification stage is disposed of by cycling it through the pulp mill chemical recovery cycle. If chlorine is used as a bleaching chemical, the effluents cannot be disposed of in the recovery plant because of the corrosiveness of chlorides and the difficulty in purging chlorides from a closed recovery cycle. White liquor, the same reagent that is used in the kraft pulping process, can also be used in the oxygen delignification process and then recycled through the recovery plant. Installation of an oxygen delignification unit may require that the capacity of the chemical and energy recovery plant be increased to accommodate the additional dissolved organic and inorganic chemicals.[13]

Several commercial oxygen delignification systems have been developed. They differ more in detail than in operating principles. These units are of two general types: 1) high consistency, and 2) medium consistency. Consistency refers to the amount of wood fiber in relation to the volume of solution in a reactor vessel. The higher the ratio of fiber to water, the higher the consistency. High consistency oxygen delignification systems use pulp slurries containing 20 to 32 percent fibers. Medium consistency is 10 to 15 percent fibers. At high consistencies, the pulp is more of a "fluff" than a fluid. The key to effective oxygen delignification systems is the ability to disperse oxygen finely enough to last for the necessary reaction time. This cannot be done efficiently with pulp consistencies of less than 6 percent because of energy considerations.

Differences among the oxygen delignification systems are mainly in the design of the reaction vessel and associated pumping and gas handling equipment. In general, the capital equipment cost is lower for a medium consistency system than for a high consistency system.[14] On the other hand, the consumption of oxygen and alkali is somewhat higher for medium consistency oxygen delignification. Medium consistency systems require a longer retention time than high consistency reactors to achieve the same degree of delignification, therefore capacity for medium consistency units must be larger to maintain the same rate of production. Medium consistency oxygen stages are often used to

[11]Ronald J. Slinn, vice president, American Paper Institute, personal correspondence, August 1988. Cost data supplied by the industry have not been verified with other sources.

[12]Croon and Andrews, op. cit., note 9, p. 1896.

[13]Springer, op. cit., note 5, p. 172.

[14]Kamyr, Inc., *Oxygen Delignification*, bull. No. KGD1801-WN1087 (Glens Falls, NY: 1987), p. 11.

Table 5-1—Oxygen Delignification Systems Installed Worldwide

Company	Location	Startup	Sequence	Capacity a.d. metric tons/day	Medium or high consistency	Hardwood or softwood
KRAFT						
Scandinavia						
Bilierud	Gruvoen, Sweden	1972	OC_DEDED	500	HC	SWD
Munksjo	Aspa, Sweden	1973	OC_DEDED	380	HC	SWD
Stora Kopparberg	Skutskaer, Sweden	1977	OC_DEDED	650	HC	SWD
MoDoCell	Husum, Sweden	1977	OC_DEDED	1,000	HC	SWD
Norrlands Skogsagares Cellulosa	Vallvik, Sweden	1978	OC_DEDED	600	HC	SWD
Stora Kopparberg	Skutskaer, Sweden	1978	OC_DEDED	650	HC	SWD
Svenska Cellulosa	Oestrand, Sweden	1980	OC_DEDED	1,000	HC	HWD/SWD
Sodra Skogsagarna	Monsteras, Sweden	1981	OC_DEDED	1,000	HC	HWD/SWD
Kopparfors	Norrsundet, Sweden	1983	OC_DE_OOD	1,000	HC	SWD
			$OC_DE_PDE_PD$		MC	
Fiskeby	Skaerblacka, Sweden	1986[a]	OC_DE_ODD	510	MC	HWD/SWD
Sodra Skogsagarna	Moerrum, Sweden	1989[a]		420	MC	SWD
		1989[a]		700	MC	HWD
				8,410		
Europe and U.S.S.R.						
Cellulose d'Aquitaine	St. Gaudens, France	1973	$OCEDED$	500	HC	HWD
ZCP	Kwidzyn, Poland	1978	OC_DEHD	600	HC	SWD
UST	Illimsk, USSR	1979	OD_CEHDED	800	HC	SWD
Zellstoff	Pols, Austria	1984	OD_CEDED	630	MC	SWD
V/O Prommash	Svetogorsk, USSR	1985	$ODEDED$	455	MC	HWD
				2,985		
Africa and South America						
Sappi	Enstra, S. Africa	1970	$ODED$	200	HC	SWD
Sappi	Enstra, S. Africa	1978	$ODED$	500	HC	HWD
Sappi	Ngodwana, S. Africa	1985	OD/CED	575	HC	SWD
Suzano de Papel e Celulose	Suzano, Brazil	1989[a]		1,365	MC	HWD
				2,640		
North America						
Chesapeake	West Point, VA	1972	C_DOD	550	HC	HWD
Eddy Forest Products	Espanola, Ontario	1977	OC_DE_OHD	500	HC	SWD
Eddy Forest Products	Espanola, Ontario	1980	OC_DEHD	500	HC	HWD
Union Camp Corp.	Franklin, VA	1981	$OCED$	800	HC	HWD
Procter & Gamble	Jlethorpe, GA	1980	OD/CD_CD	1,000	HC	SWD
Union Camp Corp.	Eastover, SC	1984	OC_DED	650	HC	HWD/SWD
Consolidated Paper	Wisconsin Rapids, WI	1980	OC_DE_OD	450	MC	HWD
Champion Internat'l	Pensacola, FL	1986	OC_DE_OD	730	MC	HWD
Champion Internat'l	Pensacola, FL	1987	OC_DE_OD	560	MC	SWD
				5,740		

Table 5-1—Oxygen Delignification Systems Installed Worldwide—Continued

Company	Location	Startup	Sequence	Capacity a.d. metric tons/day	Medium or high consistency	Hardwood or softwood
Japan						
Daishowa	Shiraoi	1975	OCEHD	550	HC	HWD
Jujo Paper	Kushiro	1975	OH	600	HC	SWD
Taio Seishi Paper	Mishima	1984	OD/CE$_p$HED	665	MC	HWD
Oji Paper	Tomakomai	1985	OH	550	MC	SWD
Chuetsu Pulp Kogyo K.K.	Sendai	1986	OCH$_p$HE$_p$D	550	MC	HWD/SWD
Taio Seishi Paper	Mishima	1986	OCEHDD	525	MC	SWD
Daishowa	Suzukawa	1986		620	MC	SWD
Oji Paper	Ebetsu	1986	OD/CEHD	650	MC	HWD/SWD
Daishowa	Shiraoi	1986		400	MC	HWD
Hokuetsu Paper	Niigata	1986	OCEHD	480	MC	HWD
Kishu Paper	Shingu	1987[a]	OCEHD			
				5,590		
SULFITE						
Hunsfos	Hunsfos, Fed. Rep. of Norway	1979	OCEHH	130	HC	HWD/SWD
Bayrische Zellstoff	Kelheim, Fed. Rep. of Germany	1979	OEDH or OE$_p$H	160	HC	SWD
Rauma-Repola	Rauma, Finland	1983	OCEDH	450	MC[b]	SWD
Celpak	Paskov, Czechoslavakia	1984	OC$_L$ED	660	HC	SWD
Hannoversche Papierfabriken	Alfeld-Gronau, Fed. Rep. of Germany	1986	OCEH	250	MC[b]	SWD
PWA Waldhof	Mannheim, Fed. Rep. of Germany	1986	PO$_p$ PO$_A$ HH[c]	185	MC	SWD
Flambeau Paper	Wisconsin, USA	1987[a]	OH	200	MC[b]	HWD
				2,035		
SPECIALTY						
Peterson & Son	Moss, Norway	1975		140	MC	SWD[d]
Korsnas Marma	Korsnas, Sweden	1984		100	MC	HWD/SWD[d]
				240		

[a]Under construction.
[b]Atmospheric recator.
[c]PO$_p$ = acid peroxide/oxygen
PO$_A$ = alkaline peroxide oxygen
[d]High yield polysulfide
[e]Screen rejects.

SOURCE: Larry Tench and Stuart Harper, "Oxygen Bleaching Practices and Benefits, An Overview," Tappi Journal, November 1987, p. 56.

achieve 35 to 40 percent delignification. Both medium and high consistency bleaching systems require efficient washing of the oxygen bleached pulp to prevent carry over of the dissolved organics into the bleaching system.

Medium consistency oxygen delignification causes less degradation of the wood fibers than high consistency systems, but because of the slower rate of delignification it is more difficult to delignify to very low kappa numbers using medium consistency. Two-stage medium consistency oxygen systems have been proposed to overcome this problem.[15] Medium consistency may have several other advantages over high consistency processes, such as:

- Massive dewatering equipment is not needed.
- Loss in pulp strength is about one-third.
- Magnesium salt protectors are not needed.
- Use of oxygen is reduced by one-fourth.
- Almost no carbon monoxide is produced.
- Little danger of explosion from gas accumulations.[16]

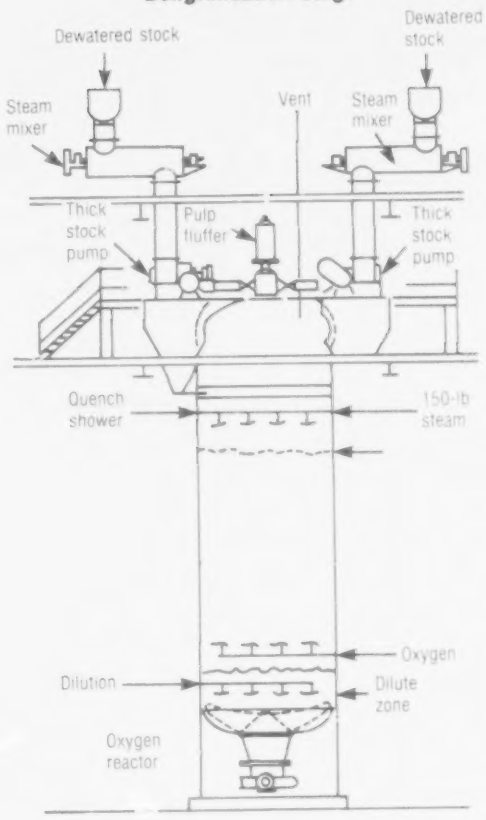
High Consistency Systems

High consistency oxygen delignification systems can produce high brightness pulps up to 90+ GE with supplemental bleaching. In the high consistency processes well-washed brownstock pulp, that is dewatered after discharge from the digester to 28 to 32 percent consistency, is treated with alkali (oxidized white liquor) and magnesium salts (a protector or inhibiter) in a mixer, it is then fluffed and fed into an oxygen reactor (figure 5-3). The pulp is heated with pressurized steam (90 to 120 °C) and oxygen gas is injected into the bottom of the reactor. The atmosphere in the reactor is maintained at about 80 percent oxygen. Gases produced by oxidation of the lignin are purged to avoid combustion. The oxygenated pulp is washed after discharge from the reactor before being sent to the bleach plant.

Medium Consistency Systems

The steps for preparing the brownstock for oxygen treatment that are used in the medium consistency process are similar to those used for high consistency oxygen delignification. Pulp consistency is adjusted to between 10 and 15 percent. Magnesium salts may or may not be added to the pulp depending on the selected procedure. Oxygen gas is dispersed throughout the pulp mixture, and steam is added to bring the mixture to a temperature of about 100 °C before it is injected at the base of the oxygen reactor (figure 5-4). The mixing of the

Figure 5-3—High Consistency Oxygen Delignification Stage

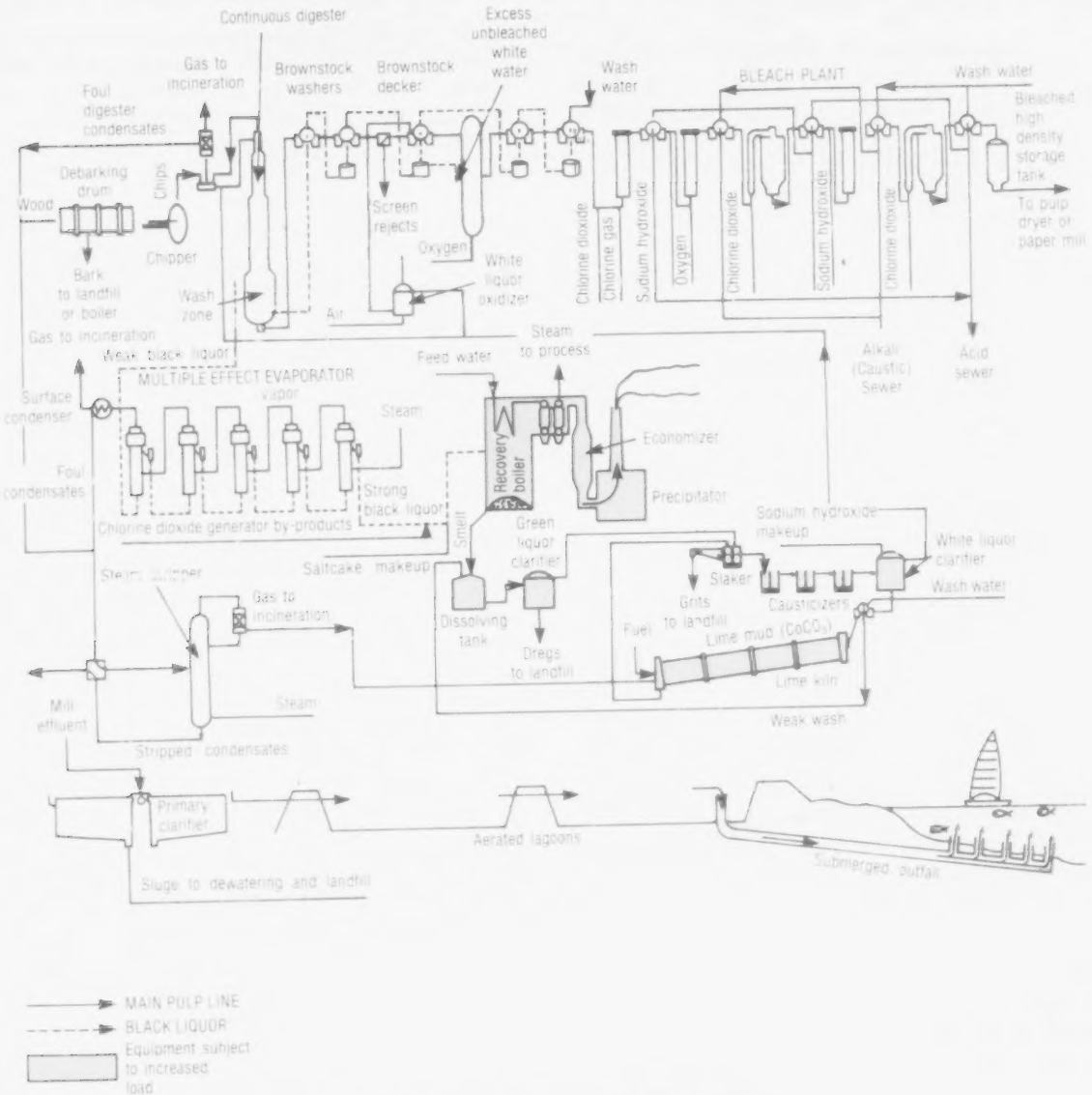


SOURCE: Adapted from Kenneth E. Smith, "Oxygen Bleaching System Operating Well at Union Camp's Franklin Mill," *Pulp & Paper*, October 1982.

[15]Ibid., p. 12.

[16]Michael D. Meredith and Joseph M. Bentvelzen, "OCOD—The Bleach Sequence of the '80s," *1984 Oxygen Delignification Symposium* (Atlanta, GA: TAPPI Press, 1984), p. 112.

Figure 5-4—Oxygen Delignification System Installed in a Bleached Kraft Pulp Mill



SOURCE: Environment Ontario, *Stopping Water Pollution At Its Source* (Toronto, Ont: Ministry of the Environment, 1988).

oxygen and steam with the pulp prior to transport to the reactor is the major difference in materials handling between the two systems. Reaction begins immediately, and about half the oxygen is consumed in the first 2 minutes. The oxygenated pulp is normally retained in the reactor for 45 to 60 minutes.

Effects of Oxygen Delignification on Pollutant Loads

The processes and conditions under which dioxins are formed during pulping, bleaching, and brightening are not well known. Dioxins are usually formed in small quantities, and the conditions leading to their formation are poorly understood. Heat, light, and catalytic action have been shown to stimulate the conversion of chlorinated precursors to dioxins.[17] Chlorine makes up about 44 percent of a TCDD molecule. Lignin is a complex polymer containing many resin acid, fatty acid, and phenolic derivatives that could serve as precursors for the formation of dioxins in the presence of chlorine under appropriate physiochemical conditions. Other non-lignin components (e.g., extractives, nonchlorinated dioxins, and catachols), may also be precursors of TCDD or TCDF.

Impco Division of Ingersoll-Rand, an equipment manufacturer that produces oxygen delignification systems, claims that oxygen treatment of prebleached pulp before a short chlorination brightening sequence significantly reduces the pollution load in kraft mill effluents compared to the most common five-stage bleach sequence CEDED (table 5-2). Similar results are reported from prebleach oxygen delignification using a chlorine-chlorine dioxide first stage bleach sequence (C_DE_OD) compared with a long bleach sequence (C_DE_ODED) without oxygen pretreatment (table 5-3). Furthermore, the total amount of chlorinated phenolic compounds formed in the bleaching process decrease considerably as a result of oxygen delignification (figure 5-5). The phenolic compounds released from conventional and oxygen-delignified pulps are lower in quantity but probably do not differ much in composition compared to those produced from conventional pulp.[18] To the extent that phenolic compounds may be linked with the production of TCDD, this may indicate that oxygen delignification could reduce the amounts of phenolic precursors present in the pulp.

Limited data are available that directly relate the reduction of TCDD and TCDF to oxygen delignification. There is substantial evidence that oxygen delignification can reduce the amount of waste chlorinated organics produced, as well as reduce BOD and COD (chemical oxygen demand), and can significantly reduce effluent color. Few analyses have been made of dioxin in effluents and pulps from oxygen-treated pulps. The Swedish Pulp and Paper Research Institute recently published some preliminary information on the effects of oxygen delignification on dioxins and furans.

Sweden's experience with oxygen delignification and appropriate bleaching sequences show that the release of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF)[19] in kraft pulp mill effluents can be reduced to relatively low levels (table 5-4). Similar reductions in PCDD and PCDF have been recorded in prebleached oxygen pulps. Conventionally bleached softwood pulps contained levels of PCDD and PCDF of between 9 and 29 ppt; oxygen pulps contained between 0.2 and 5 ppt (expressed as TEQ—toxic equivalents).[20] A similar sample of bleached pulp from five U.S. kraft mills without oxygen delignification averaged 13 ppt TCDD and 93 ppt TCDF (TEQ about 22 ppt, within the range of Swedish mills reported above).[21] One U.S. mill with a softwood oxygen delignification line and a short bleaching sequence including chlorine dioxide (C_D) in the first bleaching stage reports no detectable levels of TCDD in either bleached pulp or effluent.[22]

Extended Delignification

Alkaline digestion (cooking) and oxygen delignification are both aimed at reducing the amount of lignin in the wood pulp before it is brightened in the bleach plant. Therefore, oxygen is considered an

[17]U.S. Environmental Protection Agency, *Dioxins*, EPA-600/2-80-197 (Cincinnati, OH: EPA Industrial Research Laboratory, 1980).

[18]U. Germgard et al., "Oxygen Bleaching and Its Impact on the Environment," *1984 Oxygen Delignification Symposium* (Atlanta, GA: TAPPI Press, 1984), p. 101.

[19]PCDD and PCDF include TCDD and TCDF as well as other related isomers.

[20]Kringstad et al., op. cit., note 3, pp. 2-3.

[21]U.S. Environmental Protection Agency, *U.S. EPA/Paper Industry Cooperative Dioxin Screening Study*, EPA-440/1-88025 (Washington, DC: 1988), p. 76.

[22]U.S. Environmental Protection Agency, op. cit., note 4, p. 1.

Table 5-2—Effluent Characteristics of Oxygen-Treated Bleached Pulp and Pulp Bleached by the Common Chlorinated Bleach Processes[a] (pounds per ton)

Bleach sequence	BOD_5	COD	Color	CL^-
CEDED	10-39	80-90	180-250	60-70
OCED	10-15	40-50	30-50	30-40
Percent Difference	45-55	45-50	80-85	35-55

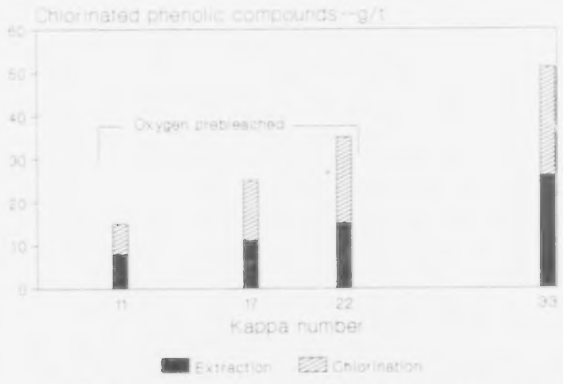
[a] Based on 50 percent delignification.
SOURCE: Ingersoll-Rand, *Oxygen Delignification Technology: An Update* (Nashua, NH: Ingersoll-Rand, 1986), p. 4.

Table 5-3—Effluent Characteristics for Softwood Kraft Pulps With and Without Oxygen Delignification[a] (kg/metric ton)

Bleach Sequence	BOD^5	COD	Color	TOCL
C_DE_ODED	15-21	65-75	200-300	5-8
OC_DE_OD	8-11	30-40	80-120	3-4
Reduction (Percent)	40-50	45-55	60-75	35-50

[a]Oxygen stage reduction in kappa number 45-50 percent.
SOURCE: Larry Tench and Stuart Harper, "Oxygen Bleaching Practices and Benefits: An Overview," *TAPPI Journal*, November 1987, p. 58.

Figure 5-5—Phenolic Compounds Formed With and Without Oxygen Bleaching



SOURCE: U. Germard et al., "Oxygen Bleaching and its Impact on the Environment," *1984 Oxygen Delignification Symposium* (Atlanta, GA: TAPPI Press, 1984), p. 101.

extension of the cooking process. Retaining the pulp in the digester for a longer period and exposing it to a modified time-temperature-alkaline cycle can reduce the amount of lignin retained in the brownstock. There is a practical limit to the amount of cooking that can be done without dissolving the desired components of the wood fiber and reducing the pulp yield. A balance, therefore, between cooking and other delignification processes must be used.

A combination of extended cooking—sometimes called "modified" cooking—and oxygen delignification has been used to achieve kappa numbers between 10 and 12 for unbleached pulp.[23] Others believe that kappa numbers as low as 7 can be achieved without loss of pulp strength.[24] With prebleached pulps of such low lignin content, it may be technically possible to eliminate the use of chlorine in the bleaching process altogether.

The standard kraft cooking procedure generally yields softwood pulp with kappa numbers between 30 and 35. Oxygen delignification can reduce the standard prebleached pulp to 16 to 20, although commercial practice is typically limited to 20 kappa because of strength considerations. Extended cooking plus oxygen treatment can produce pulps with kappa numbers between 7 and 12. By starting the kraft cook at a relatively low concentration of alkali

[23]Stig Andtbacka, "Low Kappa Pulping Followed by Oxygen Delignification," *Australian Pulp and Paper Industry Technical Association Journal*, March 1986, p. 129.

[24]Kamyr, Inc., *Kamyr Continuous Cooking Plus Modified Continuous Cooking Plus Medium Consistency Oxygen* (Glens Falls, NY: date unknown).

Table 5-4—Emissions of PCDD and PCDF (expressed as TEF)[a] in Receiving Waters From Swedish Pulp Mills With and Without Oxygen Delignification

	Pulp	Bleaching process	Production (tons/yr)	TEF (g/yr)
Without oxygen delignification				
1	Softwood	$(C_{95}+D_5)$ (E_O) H D	300,000	2-5.8
	Hardwood	$(C_{95}+D_5)$ (E_O) H D E D		
2	Softwood	C $(E_{O\text{-}P})$ H D (E_P) D	125,000	0.7
	Hardwood	$(C_{10}+D_{90})$ E D E D		
With oxygen delignification				
3	Softwood	O $(C_{85}+D_{15})$ E D E D	160,000	0.4
	Hardwood	O $(C_{70}+D_{15})$ E D E D	160,000	
4	Softwood	O $(C_{85}+D_{15})$ (E_O) D D	75,000	0.7
	Hardwood	O $(C_{70}+D_{15})$ (E_O) D D		
5	Softwood	O $(C_{85}+D_{15})$ (E_O) D E D	235,000	0.1
	Hardwood	O $(C_{70}+D_{15})$ (E_O) D E D	85,000	

[a] TEF is the "Toxicity Emission Factor" according to G. Eadon as discussed in J.S. Bellini and D.G. Barnes, *Toxicology and Industrial Health*, vol. 1, No. 4, 1985, p. 235.

SOURCE: Knut P. Kringstad et al., addendum to "Bleaching and the Environment," *1988 International Pulp Bleaching Conference*, Orlando, FL, June 5-9, 1988 (Atlanta, GA: TAPPI, 1988), pp. 2-3.

and lengthening the retention period, low-lignin pulps are produced with comparable strength to pulps containing more lignin that are produced by standard cooking methods.

Extended delignification can be either a batch process or a continuous process. Continuous modified cooking digesters have been developed by Kamyr, Inc. and others, which split the white liquor (alkali) charge and introduce it into different points in the impregnation and cooking stages and at the base of the reactor (figure 5-6).

As its name implies, extended delignification requires a longer cooking time than standard pulping. While standard kraft pulp is cooked for 1 to 3 hours, extended delignification, including impregnation (steeping) and cooking, may require over 4 hours.[25] Initial concentration of alkali in the cooking liquor is about half of that used in the standard cook. By the end of the cook, however, about 2 percent more alkali is used in the extended process than in the standard. Pilot tests have shown that pulp lignin concentration at the end of extended delignification may be 40 to 60 percent of that contained in standard pulp.

Pretreatment of Oxygen Pulps With Nitrogen Dioxide (PRENOX)

Laboratory experiments and pilot plant studies have demonstrated that treatment of pulp with a combination of nitrogen dioxide and oxygen prior to oxygen delignification can also reduce the lignin in prebleached pulps.[26] Nitrogen dioxide has been shown to promote more selective delignification in the oxygen delignification stage, thus resulting in less damage to the fiber.[27] The upper limit of delignification for most softwood kraft pulps is considered to be about 50 to 55 percent for oxygen treatment. Delignification to these limits, however, causes fiber degradation. To avoid this, oxygen delignification is generally reduced to about 40 to 45 percent. By using PRENOX before the oxygen stage, delignification rates of about 75 percent (kappa number 8-10) may be possible to achieve.[28]

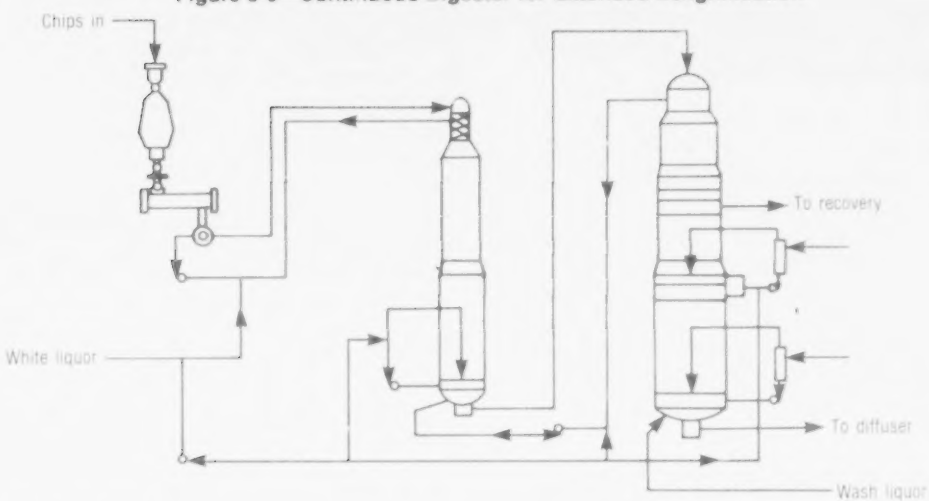
[25] Andtbacka, op. cit., note 23, p. 130.

[26] Rolf Brannland et al., "Oxidation of Pulp With NO_x/O_2 Prior to Oxygen Delignification—A Novel Process With Potentially Less Pollution," S-93E, 04/87 2000 MarknadsRadet, Reprinted by Sunds Defibrator, May 1986.

[27] D. Lachenal and C. DE Choudens, "High Efficiency Oxygen and Peroxide Delignification," *Cellulose Chem. Technol.*, vol. 20, p. 557.

[28] Bryan L. Sorensen, "New Bleach Plants: A Review of Present State of the Art," *1987 Bleach Plant Operations Seminar* (Atlanta, GA: TAPPI Press, 1987), p. 183.

Figure 5-6—Continuous Digester for Extended Delignification



SOURCE: Stig Andtbacka, "Low Kappa Pulping Followed by Oxygen Delignification," *Australian Pulp and Paper Industry Technical Association Journal*, March 1986, p. 130.

Soda-Anthraquinone/Oxygen Pulping

Although the kraft pulping process efficiently produces pulps with unmatched quality and may be used with any wood species, there are continuing efforts to develop a pulping system that eliminates sulfur chemicals from the pulping process because of the odor and environmental concerns. The most expensive capital investment in a kraft pulp mill is the chemical recovery plant. A soda-anthraquinone plant requires a similar recovery plant to that of a conventional system, however, the odor control equipment used in conventional mills is not needed.

The soda process was a forerunner of the kraft process.[29] Its major drawbacks are low pulp yields and inferior pulp quality that result from long cooking times, high temperatures, and the strong solution of sodium hydroxide needed to produce bleachable grade pulps.

The addition of small amounts of anthraquinone (AQ) to the pulping liquor are effective in accelerating the soda pulping process and improving pulp yields. Anthraquinones have also been used with kraft pulping, but a larger amount of the expensive chemical must be used to be effective and residual amounts of AQ can interfere with the chemical recovery plant. Furthermore, AQ is regulated by the Food and Drug Administration, and only small residual amounts are permitted in finished products.

Laboratory experiments with a two-stage soda/AQ-oxygen-sodium hydroxide delignification of hardwood has produced pulp of kappa numbers between 10 to 12 with about 5 percent higher pulp yields than comparable kraft pulp. Lignin content of softwoods pulped (kappa number 20) by the two-stage process did not match those of the hardwood pulp, however.[30] Researchers found that to avoid fiber degradation, the soda cooking must be stopped at a high kappa number and the remainder of delignification done with oxygen.

DISPLACEMENT BLEACHING

There is no difference between the chemistry of displacement bleaching and that used in conventional bleaching, only in the efficiency of the mass

[29]Hutch Holton, "Softwood Pulping: A Major New Process," *Pulp & Paper Canada*, vol. 78, No. 10, October 1977, p. 19.

[30]Y.C. Tsai, H-m. Chang, and J.S. Gratzl, "Optimization of Soda-AQ/Oxygen Pulping of Southern Pine," *1984 Oxygen Delignification Symposium* (Atlanta, GA: TAPPI Press, 1984), p. 31.

transfer.[31] When bleaching chemicals are displaced through a pulp mat, the fibers are continually exposed to highly concentrated bleaching chemicals, therefore bleaching is very rapid.

Displacement (sometimes referred to as "dynamic") bleaching is generally conducted in a multistage displacement tower (figure 5-7). Filtrate withdrawn at each stage is supplemented with makeup chemicals and reused. Unbleached pulp moves sequentially upward, while white liquor moves downward through the bleaching column. Displacement bleaching uses a minimum of water, thus reducing the amount of waste effluent and enabling the recycling of bleaching chemicals. The system is suited for use in a "closed-mill" configuration (see above).

Any water soluble bleaching chemical, including chlorine gas, can be used in displacement bleaching. Softwood and hardwood pulps of 86 to 88 GE brightness have been produced by displacement systems.[32] Displacement bleaching technology has produced mixed results. Although it requires more chemicals, and causes corrosion and scaling problems in some instances, displacement bleaching is still considered promising.

CLOSED-CYCLE BLEACHED PULP MILL

During the past 20 years the concept of a closed-cycle pulp mill that could significantly reduce the amount of waste effluents has received some attention. The closed-cycle concept involves:

- reducing the amount of water consumed by using filtrate as wash water,
- cycling the spent bleaching chemicals to the chemical recovery plant, and
- recovering the salts introduced into the recovery system for either re-use in manufacturing the bleaching chemicals or for disposal (figure 5-8).

By closing the water cycle of a bleached kraft mill, the demand for heat is reduced and considerable energy savings can result. Excess heat produced in the process is disposed of as low-grade waste heat into cooling waters. A closed-cycle mill bleach plant might use only 3,900 gallons per air-dry ton of pulp produced, while an average North American Mill would use 20,000 gallons.[33] A mixture of chlorine dioxide and chlorine gas is substituted for pure chlorine in the first bleaching stage to avoid reducing the pulp strength during the high-temperature chlorination (60 °C).[34]

Pulp manufacture and bleaching, being chemical processes, obey the general principles of chemical combination and mass balance. In a mill in which water and all chemicals are recycled, all of the chemicals must be kept in proper balance or either an excess or shortage of bleaching chemicals will occur. An excess of certain chemicals, particularly sodium chloride (common salt), can contribute to corrosion of the recovery boiler. Some of the recovered salt can be reused to produce chlorine dioxide, but the excess must be disposed of. Corrosion-resistant materials and careful chemical control have largely overcome these problems.

The Great Lakes Paper Co. at Thunderbay, Ontario, installed the first closed-cycle mill in 1977, but the process has not been successful, and the mill is not now operating in the closed-cycle mode. Severe operating problems have been encountered which have resulted in abandoning the process. If these problems could be overcome by further development, the closed-cycle concept might reduce the cost of biological waste treatment, reduce energy costs, increase fiber yield, decrease water usage, and reduce chemical costs.

It is possible that some variation of the closed-cycle bleached kraft mill concept could be developed to incorporate oxygen delignification, extended delignification, or displacement bleaching, thus avoiding some of the problems encountered with conventional bleaching sequences.

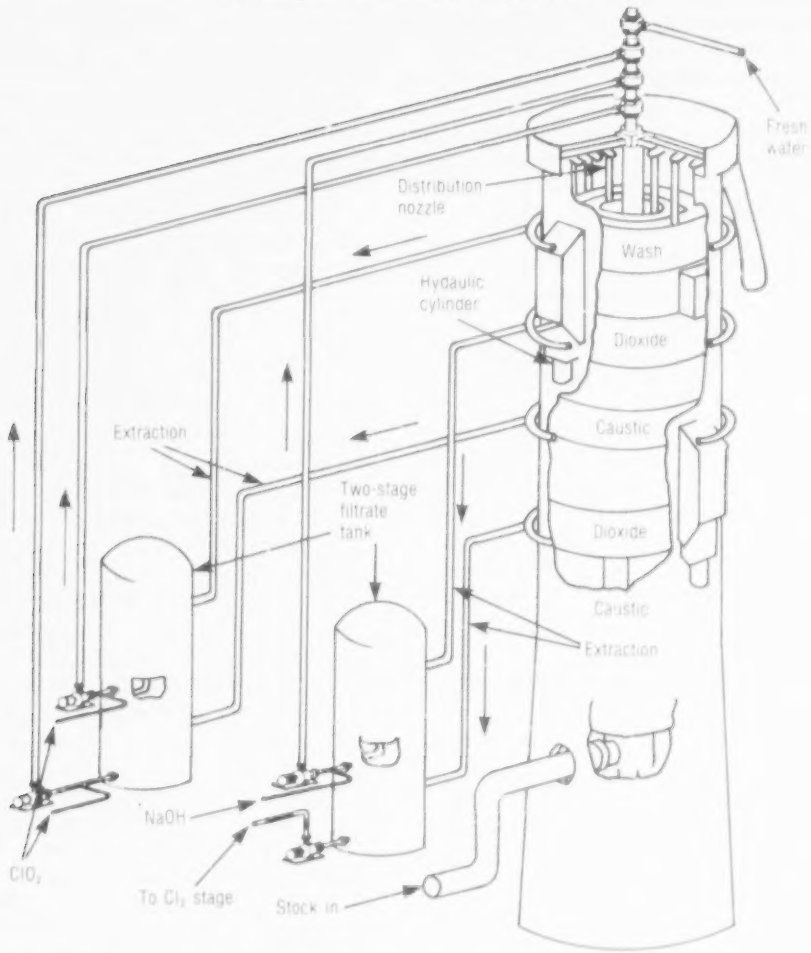
[31]Johan Gullichsen, "Displacement Bleaching," *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 276.

[32]Springer, op. cit., note 5, p. 170.

[33]W. Howard Rapson, "The Closed-Cycle Bleached Kraft Pulp Mill," *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 415.

[34]Springer, op. cit., note 5, p. 129.

Figure 5-7—Multistage Displacement Bleach System Single Tower Bleach Plant Showing an EDED Wash Sequence

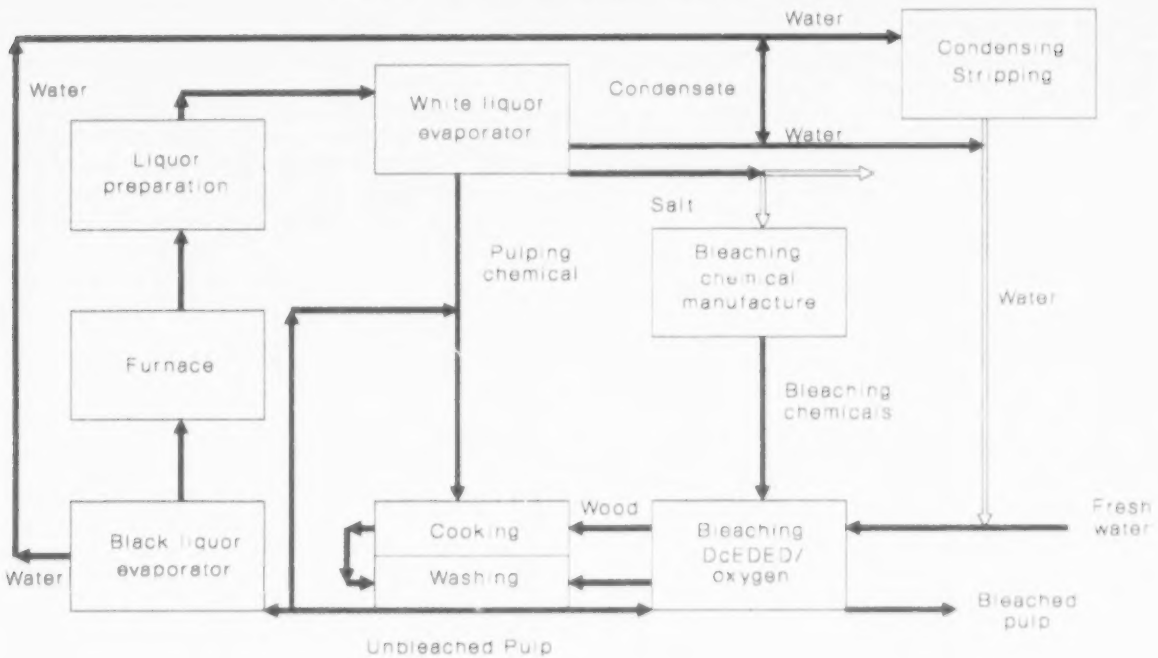


SOURCE: John Gullichsen, "Displacement Bleaching," *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 288.

WASTE-OUTLET TREATMENT TECHNOLOGIES

Several physical and chemical treatments have been developed to cleanse pulp and paper effluents. Waste treatment processes include resin separation and ion exchange; use of chemicals such as aluminum oxide, metallic ions, lime, amines, and ozone; adsorption by wood; biological treatments such as enzymes and bacteria; filtration systems such as activated charcoal; membrane separation; and ultrafiltration, irradiation, and reverse osmosis. It is technically feasible, but extremely costly, to clean pulp-mill wastes to the purity of drinking water. In judging the economics of waste treatment systems, the cost of the exotic waste treatment technologies is generally compared with the cost of secondary biological treatment, which is the U.S. industry standard for removing most foreign materials other than color.

Figure 5-8—Closed-Cycle Bleached Kraft Pulp Mill



SOURCE: W. Howard Rapson, "The Closed-Cycle Bleached Kraft Pulp Mill," *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 414.

The effectiveness of any waste treatment system is related to the internal processes used for delignifying and brightening the pulp. The load on the waste treatment plant can be reduced by using some of the technologies discussed above, e.g., oxygen delignification, soda-AQ pulping, or displacement bleaching. Use of bleaching sequences including oxygen, chlorine dioxide, hypochlorite, peroxide, or ozone can also change the nature of the treatable wastes. Waste treatment and pulping and bleaching technologies, therefore, may be considered as an integral system that can be balanced to achieve the desired performance standards.

Theoretically, the optimum way to make waste treatment a less costly venture is to integrate it into the manufacturing process. Benefits can then be gained from conservation of raw material, fibers, additives, energy, and water. Cost analyses of internal controls v. external controls generally show that internal modifications may be less capital intensive.[35] On the other hand, external pollution control does not interfere with established manufacturing processes and provides flexibility for a range of operating conditions and exigencies. Realistically, successful control probably requires a combination of both.

Color and solids are the first targets for cleanup of the pulp waste stream as it leaves the mill outlets. Untreated pulp-mill effluents are generally of a deep mahogany color. Most of that color is derived from the bleaching process, and most of that is from the caustic extraction process after the first bleaching stage. Most of the color is attributable to lignin in the waste effluent. Lignin is resistant to biodegradation.

[35]H. Gehm, *State-of-the-Art Review of Pulp and Paper Waste Management*, EPA Technology Series EPA-R2-73-184 (Washington, DC: U.S. Government Printing Office, 1973), p. 32.

and secondary biological treatment plants remove only 30 percent or less of the color component.[36]

Primary Treatment of Suspended Solids

Suspended solids in the waste stream consist of bark, fiber, fillers, clay, and coloring agents. These are removed by sedimentation, flotation, and screening. Grit chambers, screens, and chemicals are used as sediment clarifiers to remove grit. Removal of suspended solids and grit currently constitute primary (first stage) treatment of pulp and paper mill waste.

Secondary Biological Treatment

Removal of suspended solids in the first stage is generally followed by biological waste treatment that is principally aimed at reducing the BOD of treated water. Secondary biological treatment has little effect on effluent color, but it may significantly reduce levels of toxic pollutants.[37] As its name implies, biological treatment relies on the assimilation and conversion of potential pollutants in the waste effluent by bacteria, fungi, algae, and other living organisms. Since biological treatment relies on the physiological processes of living plants and animals to reduce the pollution load, the second stage of waste treatment is similar to farming—the plants and animals must be kept healthy, productive, and reproducing. In order to promote biological activity, adequate air and nutrients must be provided to the biota.

Biological treatment can remove 80 to 95 percent of the BOD. Research has shown that chlorinated bleach plant derivatives are more difficult to degrade by biological processes than nonchlorinated wastes. Several biological treatment systems are currently used to treat pulp mill waste (e.g, oxidation ponds, activated sludge, and aerated basins). Emerging biological treatment technologies include: rotating biological surfaces, fixed-film activated sludge, aerated activated carbon, and deep tank aeration.

Bench-scale wastewater treatability studies conducted by EPA indicated that the addition of alum or lime can remove more than 95 percent of TCDD and TCDF in bleach plant wastewater by improving the recovery of suspended sediments to which they adhere. Use of chemical treatments would probably require additional clarification and sludge dewatering facilities at most mills. The application of a non-ionic polymer to an oxidation pond reduced TCDD and TCDF to less than detectable levels.[38]

Oxidation Ponds

Oxidation ponds or basins depend primarily on surface exchange with the atmosphere for aeration, although some oxygen may be supplied photosynthetically by aquatic plants. Large surface areas are generally needed to provide sufficient air to maintain biological activity, therefore oxidation ponds tend to be large and shallow. Since the rate of biological activity increases with temperature, oxidation ponds work best in warmer southern climates. Oxidation ponds are relatively inexpensive, require little mechanical equipment, produce little secondary waste products that must be disposed of, and in emergencies can serve as temporary impoundments should an accidental discharge of harmful chemicals occur in the mill. Racetrack-shaped oxidation ditches are sometimes used to eliminate the primary clarification stage. Oxidation ditches require mechanical aeration because of the smaller water surface and perform more like an extended aeration activated sludge process than like a conventional oxidation pond system.

Oxidation basins are frequently equipped with aerators to increase the rate of biological activity (aerated stabilization basins). Nitrogen and phosphorous fertilizers are sometimes added if the waste stream is nutrient deficient. These supplemental treatments can reduce the retention time in the oxidation pond to 8 to 10 days in order to reduce BOD to a low level. The addition of mechanical aerators increases the cost of oxidation ponds, but they are generally cheaper than activated sludge systems.

[36]Springer, op. cit., note 5, p. 182.

[37]C.C. Walden and J.C. Mueller, *Investigation of the Effect of BOD Reduction Systems on Toxicity*, CPAR Rept. No. 150-1 (Ottawa, Ont: Canadian Forest Service, 1973).

[38]U.S. Environmental Protection Agency, op. cit., note 4, p. 9.

Activated Sludge

Activated sludge treatment systems are often used where space limits the use of oxidation ponds. An adaptation from sanitary sewage treatment, activated sludge is a high-rate biological process that can reduce waste treatment retention time to 3 to 8 hours. The biological mass that is produced in the aeration stage of the treatment process is separated in a secondary clarifier and the active biological components are returned to the process, thus further accelerating biological activity.

Activated sludge systems are flexible and can be adapted to treat a wide range of wastes. However, these systems cannot withstand shocks from emergency mill releases nearly as well as oxidation ponds, and the biological balance of the process is more sensitive to chemical and biological perturbations. The capital and operating cost of activated sludge systems are generally twice as great as aerated ponds.

The pulp and paper industry is the largest user of pure oxygen-activated sludge (UNOX) technology, with 16 plants in operation in 1986.[39] Pure oxygen systems can remove 87 to 97 percent of BOD. The process has several advantages over conventional activated sludge systems such as, smaller aeration tanks required better tolerance to "shock loading," and better sludge settling. A buildup of carbon dioxide at some UNOX plants has raised concern about the potential toxicity to fish. Retention time in pure oxygen systems is about 3 to 4 hours.

Two-stage activated sludge systems, such as the Zurn Attisholz process, using two oxygen levels sequentially with high recycling rates can reduce BOD 95 percent and the process is very stable. Cost of the two-stage process may be slightly less than with conventional activated sludge.[40] There is some evidence that the two-stage oxygen activation process is more efficient in reducing toxicity of kraft wastewater.[41]

New or Developing Treatment Technologies

A number of of coagulants that remove color have been tested. Although several are effective, e.g., alum, ferric sulfate, sulfuric acid, activated carbon, etc., they are expensive. Lime is the least costly precipitation agent, and can be reclaimed in a kraft mill by oxidizing in the lime kiln. Pretreatment of waste effluents with enzymes before precipitation with lime can increase efficiency, as can the additions of magnesium sulfate.

Fungi have also been used to remove color from wastewater. White rot fungus (*Phanerochaete chrysosporium burds*) can metabolize the lignin responsible for most of the color of wastewaters. It can also eliminate toxic chlorinated and halogenated compounds from the waste stream, including dioxins.[42] Although the process (MYCOR) is economical, the fungi culture cannot sustain itself and may collapse, thus it must constantly be recultured.

Conventional ion exchange resins have not proven technically successful in removing color from pulping and bleaching wastes, but specialized synthetic resins seem promising. Resins are sensitive to overloading from suspended solids and contaminants that reduce their effectiveness, thus they have been used primarily on both small waste streams and isolated output from the chlorination and first extractive stages of the bleaching sequence. Ion exchange resins have thus far found only limited use in the pulp and paper industry. Activated carbon, because of its large adsorption surface area, is an effective scrubbing agent. The charcoal process has been used commercially, but its high cost and regeneration requirements make it less attractive. The efficiency of membrane processes is considered good, but their costs remain high.

Rotating Biological Surface

A new developing technology, rotating biological surfaces (RBS), involves rotating polyethylene discs alternately through the wastewater and into the air as they rotate on a shaft. The process is analogous to the

[39]Springer, op. cit., note 5, p. 240.

[40]Ibid., p. 242.

[41]Waste Water Technology Center, *An Assessment of Kraft Bleachery Effluent Toxicity Reduction Using Activated Sludge*, EPS 4-WP-77-3 (Ottawa, Ont: Environment Canada, 1977).

[42]U.S. Environmental Protection Agency, *National Dioxin Study*, EPA/530-SW-87-025 (Washington, DC: 1987), p. VI-2.

simple "trickle filter" where wastewater is percolated through a porous medium exposed to air in the interstices. RBS usually operates in three stages, and removal of up to 90 percent of the BOD has been achieved with this technology. Efficiency of the process is proportional to the surface area of the discs, rotation speed, and submergence depth of the discs. Application of RBS is probably limited to small- or medium-size pulp mills because of costs in scaling the equipment to large volumes. In smaller operations the cost of RBS is about the same as the activated sludge process. Although pilot-scale testing of RBS has shown promise for removing BOD and toxicity, mill-scale studies have encountered operating difficulty.[43]

Innovations in Activated Sludge Technology

High-Rate, Fixed-Film Activated Sludge—Solid particles (e.g., clays, sand, or calcium carbonate) added to activated sludge systems can improve sludge settling and prolong solids retention. Calcium carbonate has been particularly effective because of its buffering capacity with regard to acid components in the waste effluent. The particles develop a fixed-film growth, allowing a high level of biological growth to develop on the expansive particle surfaces. Preliminary studies indicate that nearly all of the solids can be retained in the system except a small amount that is lost with the treated water. Most of the solids are lost through the respiratory processes as carbon dioxide and water.

The oxitron process is a variation of the fixed-film activated sludge system. Effluent, free of suspended solids, is fed to a fluidized bed of sand through which pure oxygen is injected. Biological growth develops around the sand particles, finally causing them to rise in the fluidized bed where they are selectively removed. The sand is later cleaned of the growth and returned to the fluidized bed. Tests of the process show it to be efficient and compact, but it is unable to tolerate any solids in the wastes to be treated. The oxitron system is best suited for large waste volumes of 2 to 3 million gallons daily. There are no commercial installations in service, but new technologies may utilize elements of the process.

Aerated Activated Carbon Filter—Experiments have shown that due to its immense surface area activated charcoal is an efficient filter medium. Coarse granular charcoal placed in a filter bed has been shown to be effective in removing contaminants from waste effluent. To keep the system aerobic, air is pumped through the filter bed. The system is tolerant of excessive suspended solids, but the capital and operating costs are likely to be high. While the system has been used on sanitary wastes, there has been limited operating experience in the pulp and paper industry.

Captor System—An English innovation, the Captor System is similar to the conventional diffused-aeration activated sludge process, but it encapsulates the biological growth in small polyurethane sponges. With the biomass contained in the sponges, the treated effluent is discharged through a screen sized to retain the impregnated sponges. Sponges are cleaned for reuse by squeezing through a wringer. Developers claim that a secondary clarifier is not needed, therefore the plant size may be reduced by about 20 percent from that of a conventional activated sludge plant. The Captor System has been used for municipal wastes, but it is not certain that this treatment would be sufficient to meet U.S. water standards. It may prove useful in upgrading existing overloaded biological treatment systems.

Deep Tank Aeration—Deep tank aeration increases the amount of time that air is in contact with the waste effluent. As its name implies, the process uses a deep tank or deep shaft as an aeration chamber. This eliminates the need for a secondary clarifier but still requires a floating clarifier. Deep aeration occupies less space than conventional activated sludge systems and is capable of handling emergency "shock" loads from the paper mill.

Anaerobic Treatment

Anaerobic waste treatment is neither new, nor innovative. However, with reduced water usage by many of the modern pulp mills, there has been a general increase in the potency of the pollution load, and anaerobic treatment is being reconsidered as a means to improve waste treatment. Anaerobic systems are well suited for treating high-strength waste,

[43]U.S Environmental Protection Agency, *Development Document for Effluent Limitations Guidelines and Standards for the Pulp, Paper, and Paperboard and the Builders' Paper and Board Mills Point Source Categories*, EPA 440/1-82/025 (Washington DC: 1982), p. 342.

but with modifications such as, attached-film and expanded bed reactors, it may also be possible to treat low-strength waste anaerobically as well.

Anaerobic (absence of oxygen) decomposition is a microbial process, which is primarily dependent on bacteria. Unlike aerobic processes (e.g., activated sludge and oxidation ponds to which air is supplied) anaerobic processes depend on bacterial action that obtains oxygen from sulfate and nitrate ions in the waste stream. When applied in the pulp and paper industry, anaerobic treatment is generally used as a waste pretreatment before release to the aerobic stages of the treatment process. Anaerobic systems are sensitive to imbalances in the ambient waste, but the process is durable and can be applied to a wide range of waste effluents. High temperatures are needed to reduce treatment time, long startup periods are required, odor emissions can be significant, and there is difficulty in achieving low BOD levels with anaerobic decomposition.

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